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SOLUBILITY ISOTHERM AT 30.5° OF THE TERNARY SYSTEM
LiOH-H₂O₂-H₂O AND A STUDY OF LITHIUM PEROXIDE HYDRATE

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A study of the solubility of the ternary system LiOH-H₂O₂-H₂O at 10, 0, -10, and -21° with the composition of the solid phases determined by the residue method made it possible to establish the existence of the lithium peroxide perhydrates with the compositions Li₂O₂·H₂O₂·3H₂O, Li₂O₂·H₂O₂·2H₂O and Li₂O₂·2H₂O₂ [1]. No hydrated forms of lithium peroxide were detected under these conditions. Investigations of lithium peroxide perhydrates showed that these compounds are unstable and readily lose hydrogen peroxide of crystallization on heating [2] and in vacuum at room [3] and slightly elevated temperatures [4]. In actual fact, with a rise in temperature, the region of existence of lithium peroxide perhydrates in the system LiOH-H₂O₂-H₂O decreases in accordance with the thermal stability of these compounds [1]. Therefore, at higher temperatures one might expect the formation of either lithium peroxide or its hydrated forms as solid phases in the system LiOH-H₂O₂-H₂O. With this aim, we studied the solubility isotherm at 30.5°.

EXPERIMENTAL

The solubility in the system LiOH-H₂O₂-H₂O at 30.5° was studied in a water thermostat with a contact thermometer, which regulated the temperature with an accuracy of ±0.2° by means of a mercury relay. When a sample was removed, the vessel for removal of the sample was also placed in the thermostat. The removal of a sample and analyses of the liquid phase and "residue" for active oxygen and lithium oxide were carried out by the procedures we used for studying the system LiOH-H₂O₂-H₂O at low temperatures [1]. The composition of solid phases formed in the system was determined by the residue method. The time required for the equilibrium state to be established in the system was first determined by a graphical method with a constant active oxygen content in the liquid phase and in the presence of an equilibrium solid phase of definite composition. Equilibrium was reached after 1-1.5 hr at 30.5°.

Data on solubility in the system LiOH-H₂O₂-H₂O at 30.5° are given in Table 1 and are presented graphically on a triangular diagram in Fig. 1, and also in a system of rectangular coordinates (Fig. 2). The solubility of LiOH·H₂O at 30.5° is 6.83% of Li₂O or 10.95% of LiOH.

It was established that the following solid phases exist in the system LiOH-H₂O₂-H₂O at 30.5°: LiOH·H₂O, Li₂O₂·H₂O, Li₂O₂·H₂O₂·3H₂O, Li₂O₂·H₂O₂·2H₂O and Li₂O₂·2H₂O₂. The solid phase LiOH·H₂O exists at 30.5° over the range of hydrogen peroxide concentrations in the liquid phase from 0 to 1.63% (0-0.77% of active oxygen). In the region of low H₂O₂ concentrations in the liquid phase at 30.5°, we detected the formation of a new solid phase of the type Li₂O₂·H₂O, which does not exist in the system LiOH-H₂O₂-H₂O at -21, -10, 0, and 10° [1]. The solid phase Li₂O₂·H₂O exists over a narrow range of hydrogen peroxide concentrations in the liquid phase from 1.63 to 6.17% (or 0.77-2.90% of act. O₂), but on the diagram (Fig. 2) a definite, clearly expressed branch of the solubility curve corresponds to it.

TABLE 1

Data on Solubility in the System $\text{LiOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ at 30.5°

Number in order	of ex- peri- ment	H ₂ O ₂ conc. in weight %		Composition of liquid phase in weight %				Composition of solid residue in weight %			Solid phases	Comments
		H ₂ O ₂	O ₂	act. O ₂	H ₂ O ₂	Li ₂ O	H ₂ O	act. O ₂	Li ₂ O	H ₂ O		
1	10	4.60	0.75	0.55	1.17	6.49	92.96	0.13	28.06	71.81	LiOH·H ₂ O	Starting materials
2	9	2.51	1.18	0.99	2.10	6.75	92.26	0.45	27.19	72.36	LiOH·H ₂ O	LiOH·H ₂ O + H ₂ O ₂
3	8	5.81	2.73	0.77	1.63	5.34	93.89	6.77	29.73	63.50	LiOH·H ₂ O + Li ₂ O ₂ ·H ₂ O	The same
4	3	8.46	3.98	1.17	2.49	4.19	94.64	24.01	42.77	33.22	Li ₂ O ₂ ·H ₂ O	»
5	4	13.66	6.42	2.90	6.17	5.80	91.30	23.09	41.21	35.70	Li ₂ O ₂ ·H ₂ O	»
6	7	28.11	13.21	3.47	7.38	3.29	93.24	17.68	16.53	65.79	Li ₂ O ₂ ·H ₂ O ₂ ·3H ₂ O	»
7	2	22.57	10.61	3.76	7.99	4.53	91.71	16.67	15.05	68.28	The same	»
8	12	34.15	16.05	9.02	19.18	4.36	86.62	18.26	17.67	64.07	»	»
9	11	39.47	18.55	10.17	21.62	4.36	85.47	18.54	14.41	67.05	»	»
10	1	44.26	20.80	10.42	22.15	4.35	85.23	23.08	19.63	57.29	»	»
11	16	22.13	10.40	12.72	27.04	5.59	81.64	22.29	18.89	58.82	Li ₂ O ₂ ·H ₂ O ₂ ·3H ₂ O + + Li ₂ O ₂ ·H ₂ O ₂ ·2H ₂ O	Li ₂ O ₂ ·H ₂ O ₂ ·2H ₂ O + + H ₂ O ₂
12	13	30.17	14.18	16.38	34.82	5.56	78.06	23.55	18.34	58.11	The same	The same
13	5	59.84	28.12	21.19	45.05	5.51	73.30	23.82	15.98	60.20	LiOH·H ₂ O + H ₂ O ₂	LiOH·H ₂ O + H ₂ O ₂
14	14	49.84	23.42	21.61	45.94	6.06	72.33	25.54	19.62	54.84	The same	Li ₂ O ₂ ·H ₂ O ₂ ·2H ₂ O + H ₂ O ₂
15	21	53.01	24.91	24.38	51.83	6.25	69.37	25.67	14.24	60.09	»	The same
16	17	60.44	28.41	25.29	53.77	6.79	67.92	26.29	14.65	59.06	»	»
17	18	65.40	30.74	27.45	58.36	6.96	65.59	28.30	16.02	55.88	»	»
18	19	70.14	32.97	27.99	59.51	6.72	65.29	34.28	12.69	53.03	Li ₂ O ₂ ·2H ₂ O ₂	»
19	20	75.10	35.30	30.37	64.57	5.77	63.86	37.84	14.79	47.34	Li ₂ O ₂ ·3H ₂ O ₂	»

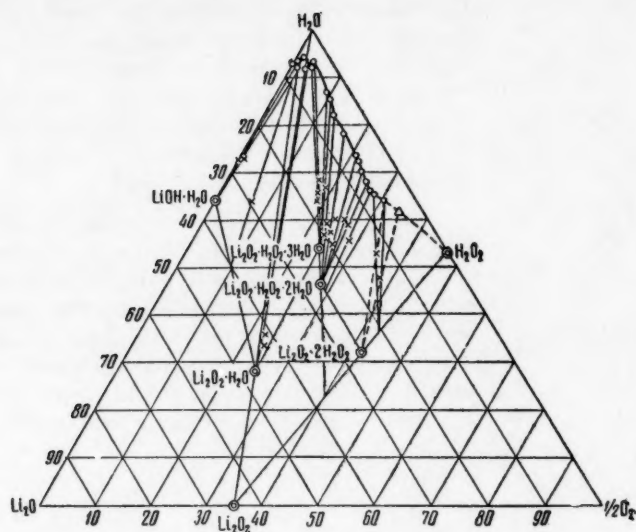


Fig. 1. Isotherm at 30.5° of the system LiOH-H₂O₂-H₂O.

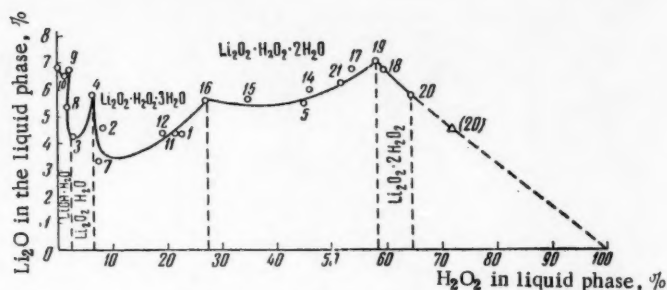


Fig. 2. Isotherm at 30.5° of the system LiOH-H₂O₂-H₂O.

At 30.5°, the solid phase $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ occupies a region of 28.65% of H_2O_2 (from 6.17 to 34.82% H_2O_2) and the solid phase $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ —24.69% (from 34.82 to 59.51% H_2O_2). The action of H_2O_2 at concentrations of 70 and 75% on $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ resulted in the formation of lithium peroxide diperhydrate $\text{Li}_2\text{O}_2 \cdot 2\text{H}_2\text{O}_2$, which exists in the system at an H_2O_2 content in the liquid phase of 59.51 to 61.57%. The solubility in the system $\text{LiOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ at 30.5° was studied up to 64.57% of H_2O_2 (or 30.37% of act. O_2) in the liquid phase.

The action of hydrogen peroxide with a concentration of more than 75% on $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ at 30.5° resulted in strong heat evolution and in a number of cases the reaction mixture was ejected from the vessel. In the region of high hydrogen peroxide concentrations there was strong decomposition of the liquid phase and displacement of the residue tie-lines to the right of the point representing $\text{Li}_2\text{O}_2 \cdot 2\text{H}_2\text{O}_2$. The probable course of the tie-lines in this region (experiments 18 and 20) is shown by broken lines in the diagram in Fig. 1; their points of intersection with the solubility isotherm in experiments 18 and 20 coincide. This is shown by a triangle in Figs. 1 and 2. The action of hydrogen peroxide of low and average concentrations (20-30% H_2O_2) on $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ at 30.5° in some cases was accompanied by an increase in the H_2O_2 concentration in the liquid phase in comparison with the original hydrogen peroxide (Table 1, experiments 15 and 16). It is evident that on reacting with $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, 20-30% H_2O_2 partly eliminates hydrogen peroxide from it.

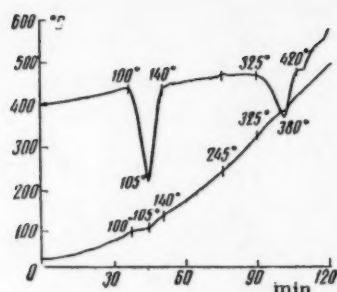


Fig. 3. Heating curve of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

H_2O samples were obtained at room temperature by the Debye method in an RKV-36 camera with copper radiation with a nickel filter.

Lithium peroxide hydrate $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$, obtained synthetically, was investigated by means of differential thermal analysis. The differential heating curve of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$, which is given in Fig. 3, differs from heating curves obtained previously for lithium peroxide perhydrates $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Li}_2\text{O}_2 \cdot 2\text{H}_2\text{O}_2$ [2]. The differential heating curve of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ differs from that of anhydrous lithium peroxide [5] in a large endothermal effect beginning at 100° and connected with the removal of water of crystallization from $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

Investigation of the decomposition of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ showed that when heated to 100° , lithium peroxide monohydrate loses water and gives anhydrous Li_2O_2 . The endothermal effect beginning at 325° corresponds to decomposition of Li_2O_2 [5]. The polymorphous conversion of Li_2O_2 at $225\text{--}235^\circ$ was weakly expressed on the heating curve of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$. The individuality of the compound $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ was also confirmed by a qualitative x-ray phase analysis, carried out by G. A. Gol'der. X-ray diffraction patterns of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ samples were obtained at room temperature by the Debye method in an RKV-36 camera with copper radiation with a nickel filter.

TABLE 2

Data on Interplanar Distances for $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$

No.	Intensity	d in Å	No.	Intensity	d in Å	No.	Intensity	d in Å
1	Av.	3,76	7	S.	2,19	13	Av.	1,26
2	Av.	2,92	8	W.	2,03	14	W.	1,19
3	V.w.	2,78	9	S.	1,83	15	S.	1,01
4	S.	2,67	10	Av.	1,72	16	Av.	0,987
5	V.s.	2,51	11	V.s.	1,55	17	W.	0,951
6	Av.	2,28	12	V.s.	1,32	18	S.	0,903
						19	S.	0,858

The data obtained for the interplanar distances of the compound $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ are given in Table 2.

The author would like to thank S. Z. Makarov for valuable advice on the work presented.

SUMMARY

1. Study of the solubility of the ternary system $\text{LiOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ with the composition of the solid phases determined by the residue method at 30.5° made it possible to establish the existence of the previously unknown hydrate form of lithium peroxide $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

2. We did not detect the lithium peroxide hydrate with the composition $\text{Li}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, which has been reported in the literature [6].

3. The individuality of the compound $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ was confirmed by differential thermal and qualitative x-ray phase analysis.

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ADSORPTION PROPERTIES
OF CARBON ADSORBENTS. COMMUNICATION 5.
PECULIARITIES IN THE SORPTION
OF WATER VAPOR BY ACTIVE CARBONS
AT HIGH RELATIVE PRESSURES

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The peculiar form of isotherms for the sorption and desorption of water vapor on active carbons has been the subject of many investigations, especially in our laboratory [1-5]. The concave initial section of the isotherm, changing into the steep rise of the sorption branch, usually with a subsequent change in the slope of the curve at high relative pressures, indicates the complexity of the sorption process. This is also indicated by the noncoincidence of the sorption and desorption branches of the isotherm, i.e., the formation of a hysteresis loop, extending over degrees of filling representing small fractions of a statistical monomolecular adsorption layer.

According to our investigations, the main region of the rise on the sorption branch of the isotherm corresponds to monomolecular adsorption [3, 5]. The concave character of the isotherm is due to the peculiar mechanism of adsorption of water molecules on the primary adsorption centers — surface oxides of carbon — as a result of the appearance of hydrogen bonds, when each adsorbed water molecule becomes a secondary adsorption center, capable of holding other water molecules through hydrogen bonds. As a result, two-dimensional islands of adsorbed water molecules are formed around the primary adsorption centers; the increase in the total number of adsorption centers due to the adsorbed water molecules themselves leads to the sharp increase in adsorption with an increase in the equilibrium pressure, i.e., to the sharp rise of the adsorption branch of the isotherm [3, 5].

The formation of a close-packed monolayer as a result of merging of the two-dimensional islands and subsequent polymolecular adsorption apparently leads to filling of the micropores of active carbons, mainly as a result of joining of the adsorption layers on opposite walls of the micropores [2]. In the region of high relative pressures, polymolecular adsorption may be complicated by capillary condensation of water vapor when the active carbon has a favorable porous structure.

In the general case, active carbons are characterized by a polymodal distribution of pore volume with respect to effective radius and contain three varieties of pore: micropores, transitional pores, and macropores [6]. Only the first two varieties of pore are important in sorption as adsorption on the surface of macropores is negligibly small due to their low specific surface ($0.5\text{--}2\text{ m}^2/\text{g}$). The micropores of active carbon of the first structural type [7] are comparable in order of magnitude to the dimensions of the molecules adsorbed and their effective radii usually do not exceed 10 Å. If adsorption occurs under the action of dispersion forces, then the adsorption potentials in the micropores are much higher due to superposition of the fields of the opposite walls of the pores.

In the final stage of the adsorption of vapor of organic substances, the micropores of active carbons are filled with liquified vapor due to merging of the adsorption layers on opposite walls of the pores; polymolecular adsorption layers are formed on the surface of transitional pores. At higher equilibrium pressures, there occurs capillary condensation of vapor in transitional pores of active carbons, which also leads to complete filling of this variety of pore by liquified vapor.

A peculiarity of the adsorption of water vapor by active carbons is the practical absence of an increase in the adsorption potentials in micropores as the forces causing adsorption (hydrogen bonds) are similar in nature to chemical forces. For this reason, the filling of the volume of the micropores must occur at relatively high equilibrium pressures. However, there is still the problem of the possibility of capillary condensation of water vapor in transitional pores of active carbons, as the limiting sorption volumes practically coincide with the volumes of the micropores according to experimental data [1]. On the other hand, in the sorption of the vapor of organic substances, such as benzene, the difference between the limiting sorption volumes and the volumes of the micropores gives the volume of the transitional pores of the active carbons.

The main problem of the present work was to investigate the sorption of water vapor by active carbons with different porous structures to determine the possibility and conditions for capillary condensation of water vapor in transitional pores.

EXPERIMENTAL

The subjects for investigation were a series of active carbon samples of the first structural type, whose transitional porosity was developed to different extents. All these carbons were obtained under laboratory conditions. Among them, P1-P5 were granulated active carbons from plant material, G1-G4 were granulated active carbons from mineral carbons, and AU-10-AU-14 were samples of active carbons with developed transitional porosity, which were described and studied in detail in previous work [8].

For determination of the main parameters of the porous structure for samples P1-P5 and G1-G4, a detailed investigation was made of the sorption and desorption isotherms for benzene vapor at 20° over a wide range of equilibrium relative pressures from $1 \cdot 10^{-5}$ to unity. The experiments were carried out on a normal apparatus with quartz sorption balances. The carbons were first evacuated with a three-stage mercury pump for 6 hr at 450° to a residual pressure of $\sim 1 \cdot 10^{-6}$ mm. The establishment of the sorption equilibrium was carefully controlled.

The sorption and desorption isotherms for benzene at 20° and nitrogen at -195° [8] for samples of active carbons AU-10 — AU-14 were studied particularly carefully. The adsorption apparatus was described in detail in [9]. The conditions for preliminary evacuation of the carbons were the same as above. The results of the measurements are the equilibrium sorption values.

The main parameters of the porous structure of active carbons of series P and G were obtained from sorption and desorption isotherms for benzene vapor. The equation of the adsorption isotherm for adsorbents of the first structural type [7] corresponded to the experimental data over a wide range of equilibrium pressures. The mean values for the upper and lower limits of the range in relative pressure units were from $2 \cdot 10^{-5}$ to $7 \cdot 10^{-2}$. The constants of the adsorption isotherm equation were measured over the following ranges: limiting volumes of the adsorption space W_0 , 0.19 to 0.56 cc/g and of the constant B from $0.38 \cdot 10^{-6}$ to $1.27 \cdot 10^{-6}$.

The points at the beginning of hysteresis corresponded to equilibrium relative pressures $h_0 = p/p_s$, which practically coincided with the value $h_0 = 0.175$ within the limits of accuracy of the graphical determination. The sorption values a_0 for the equilibrium pressure h_0 were the upper limits of the adsorption component of the sorption process. For the range of sorption values from the limiting value a_s at $h = 1$ to a_0 at $h_0 = 0.175$, the method in [10] was used to calculate the specific surfaces of the adsorption films in the transitional pores s^* , which practically coincide with the specific surfaces of the transitional pores s . The isotherm for the adsorption of benzene vapor at 20° on nonporous carbon black with spherical particles, which had first been fired in vacuum at 950° and had a specific surface $s = 108 \text{ m}^2/\text{g}$, was used to determine the adsorption of benzene vapor per unit surface of carbon black $A_0 = 4.17 \cdot 10^{-3} \text{ mmole/m}^2$ for an equilibrium pressure $h_0 = 0.175$ [11]. From these data we calculated the volumes of the micropores v_{mi}^c of active carbons, corrected for adsorption in transitional pores [6]:

$$v_{mi}^c = (a_0 - A_0 s^*) v, \quad (1)$$

where $v = 0.0888 \text{ cc/mmole}$ is the volume of 1 millimole of liquid benzene at 20°. The difference between the limiting sorption volume $v_s (h = 1)$ and the corrected volume of the micropores v_{mi}^c gave the corrected volume of the transitional pores of the active carbon v_t^c (2):

$$v_t^c = v_s - v_{mi}^c. \quad (2)$$

TABLE 1

Volumes of Micropores and Transitional Pores of Active Carbons

Active carbon	a_0 in mmole per g	S_t in m ² /g	v_{mi}^c in cc/g	v_t^c in cc/g	v_s in cc/g
P1	2,91	60	0,236	0,133	0,369
P2	3,17	64	0,258	0,127	0,385
P3	2,31	84	0,174	0,277	0,451
P4	2,40	118	0,170	0,519	0,689
P5	6,07	88	0,507	0,158	0,665
G1	3,05	46	0,254	0,275	0,529
G2	2,45	57	0,197	0,191	0,388
G3	3,87	48	0,326	0,082	0,408
G4	3,66	33	0,314	0,063	0,397

The results of the calculations are given in Table 1.

Among the active carbons studied, samples G3 and G4 were characterized by low development of the transitional porosity. For carbons P1, P2 and P5, the volumes of the transitional pores were more appreciable and corresponded to substantial fractions of the micropore volumes (31-52%). The other samples, P3, P4, G1 and G2 were active carbons with a developed transitional porosity; for them, the volumes of the transitional pores either practically equaled the volumes of the micropores (G1 and G2) or considerably exceeded them (P3 and P4). Thus, the porous structure of the active carbon samples chosen for the investigation varied over a wide range.

For investigation of the sorption and desorption isotherms for water vapor at 20° we used sorption balances. The preliminary evacuation conditions were the same as those described for experiments with benzene. With each change in pressure in the system, there was no visible increase in weight of the adsorbent sample after 1-3 hr. It should be noted that in the region of higher pressure, a relatively longer time was required for the determination of each point on the sorption isotherm.

The forms of the sorption and desorption isotherms for water vapor studied could be divided into two characteristic types according to their peculiarities. An example of the first type is the isotherm for carbon P2, illustrated in Fig. 1. A characteristic of isotherms of this type is the considerable change in slope of the isotherm branches after the region of the sharp rise, which gradually become flatter. In the range of high relative pressures, the sorption and desorption branches form a hysteresis loop of considerable area. Thus, the sorption isotherm examined appears to consist of two parts with steeper branches for the first and flatter branches for the second. The sorption isotherms for carbons P1, P3 and P4 are also of the same type.

An example of the second type is the isotherm for carbon G4, which is illustrated in Fig. 2. Here, the sharp rise of the isotherm branches is appreciably displaced toward higher relative pressures. The considerable change in the slope of the branches in the range of medium sorption values, which is characteristic of the first type, is absent. The area of the hysteresis loop is considerable and the loop extends over almost the whole of the isotherm. The hysteresis loop gradually broadens with the rise in the isotherm branches. The sorption isotherms for carbons G3 and P5 are also of this type. The sorption isotherms for carbons G1 and G2 occupy an intermediate position between isotherms of types one and two.

Sorption of water vapor by the active carbons examined occurs both on the surface of the micropores and on the surface of the transitional pores. For considering the nature of the filling of micropores and transitional pores of the active carbons at limiting sorption ($h = 1$), it is advantageous to compare the limiting sorption volumes of the active carbons v_s for benzene and water. In calculating them from the formula

$$v_s = a_s v \text{ cc/g} \quad (3)$$

we used the volumes of one millimole of liquid, corresponding to tabular values for their densities in the bulk phases. The limiting sorption volumes are compared in Table 2.

According to the data in the table, the limiting sorption volumes for water are considerably less than those for benzene and the differences between them Δv_s are comparable with the volumes of the transitional pores of the carbons v_t^c (Table 1). This indicates that with limiting sorption of water vapor, only the micropores of the carbon are filled with liquified vapor throughout the volume, while the surface of the transitional pores is covered with only a polymolecular layer, corresponding to a relative pressure of unity. To check this hypothesis, it is necessary to calculate the sorption volumes for water in the micropores v_s^{mi} at limiting sorption by subtraction of the volume of the polymolecular adsorption films on the surface of transitional pores of the active carbons from the limiting sorption volumes v_s and compare the values of v_s^{mi} obtained with the volumes of the micropores themselves v_{mi}^c . To calculate the sorption volumes of water in the micropores, we used the formula:

$$v_s^{mi} = (a_s - A_s S_t) v \text{ cc/g}, \quad (4)$$

TABLE 2

Limiting Sorption Volumes

Active carbon	v_s in cc/g		Δv_s in cc/g
	C_2H_6	H_2O	
P1	0,369	0,269	0,100
P2	0,385	0,286	0,099
P3	0,451	0,223	0,223
P4	0,689	0,203	0,486
P5	0,665	0,548	0,117
G1	0,529	0,270	0,259
G2	0,388	0,228	0,160
G3	0,408	0,314	0,094
G4	0,377	0,338	0,039

TABLE 3

Volumes of Sorbed Water in Micropores and Volumes of Micropores of Active Carbons

Active carbon	a_s in mmole/g	S_t in m^2/g	v_s^{mi} in cc/g	v_{mi}^c in cc/g
P1	14,88	60	0,245	0,236
P2	15,80	64	0,260	0,258
P3	12,63	84	0,195	0,174
P4	11,26	118	0,157	0,170
P5	30,45	88	0,514	0,507
G1	14,92	46	0,250	0,254
G2	12,65	57	0,206	0,197
G3	17,37	48	0,294	0,326
G4	18,78	33	0,325	0,314

where A_s is the limiting value of water vapor adsorption in mmole/ m^2 per unit surface of transitional pores and s_p is the specific surface of the transitional pores. The value A_s may be determined from experiments on the adsorption of water vapor at 20° on nonporous channel black which has first been fired at 950° in vacuum, i.e., at the same temperature as the activation of carbons by gases (CO_2 and H_2O). It may be assumed that active carbons and the black do not differ substantially as regards the nature of the surface.

For the black with $s = 103 m^2/g$, which was used in [2], the limiting sorption of water vapor at 20° ($h = 1$) was $a_s = 2.21$ mmole/g. Hence the limiting adsorption per unit surface of adsorbent A_s is given by the expression

$$A_s = \frac{2,21}{103} = 2,14 \cdot 10^{-2} \text{ mmole}/m^2$$

The calculated sorption volumes of water in the micropores of active carbons v_s^{mi} are compared with the volumes of the carbon micropores v_{mi}^c in Table 3.

According to the data in Table 3, the volumes of sorbed water in the micropores practically coincide with volumes of the micropores of active carbons. Thus, under the sorption conditions described and at a relative pressure of unity, adsorbed water in the form of a liquid with a density which does not differ appreciably from the density of water in the bulk phase completely fills the micropores of the activated carbon; only a polymolecular adsorption layer is formed on the surface of the transitional pores.

This conclusion drawn from experiment is far from obvious from the point of view of the theory of capillary condensation. In principle, when an adsorption layer is present there should be wetting of the walls of transitional pores with the formation of concave menisci. Under these conditions, the capillary condensation of water vapor in transitional pores is unavoidable. In principle, we cannot exclude the possibility that, for some reason, capillary condensation of water vapor in transitional pores of active carbons proceeds very slowly and we did not observe this process under the measurement conditions adopted. In other words, in our experiments we did not reach true sorption equilibrium. This conclusion made it necessary to carry out special experiments of considerable duration.

As subjects for the investigation we used active carbon samples AU-10-AU-14, which had been prepared under laboratory conditions and whose adsorption properties and porous structure elements had been studied very carefully in [8]. Table 4 gives information on the volumes of the micropores and transitional pores of the active carbons according to experiments on the adsorption of nitrogen at -195° and benzene vapor at 20°. W_0^c denotes the limiting volumes of the adsorption space, which are the constants of the adsorption isotherm equation for the experimental isotherms, corrected for adsorption in the transitional pores [8]. These values practically coincide with the corrected volumes of the micropores v_{mi}^c , calculated from the adsorption at the beginning of hysteresis [8], and thus we have quite reliable data on the volumes of the micropores of these active carbons of the first structural type, which are accessible to benzene and nitrogen molecules, respectively. The micropores of these carbons are very small, as is indicated by the low values of the constant B in the adsorption isotherm equation,

TABLE 4

Volumes of Micropores and Transitional Pores of Active Carbons

Active carbon	Benzene				Nitrogen			
	W_0^c in cc/g	v_{mi}^c in cc/g	v_t^c in cc/g	v_s in cc/g	W_0^c in cc/g	v_{mi}^c in cc/g	v_t^c in cc/g	v_s in cc/g
10	0,150	0,149	0,406	0,555	0,170	0,171	0,325	0,496
11	0,175	0,175	0,482	0,657	0,188	0,193	0,442	0,635
12	0,180	0,182	0,741	0,923	0,198	0,202	0,643	0,843
13	0,142	0,143	0,723	0,866	0,175	0,173	0,687	0,860
14	0,128	0,125	0,756	0,888	0,141	0,132	0,655	0,787

TABLE 5

Distribution of Volumes of Sorbed Water in the Form of Liquid of Normal Density Between Micropores and Transitional Pores at Limiting Sorption

Active carbon	Water		v_{mi}^c in cc/g	v_t^c in cc/g	S_t in m ² /g	$v_s^{H_2O} - v_{mi}^c$ in cc/g	v_t in cc/g	$v_s^{H_2O} - v_{mi}^c$ v_t^c
	a_s in mmole/g	v_s in cc/g						
10	12,18	0,219	0,160	0,365	90	0,059	0,035	0,10
11	15,21	0,274	0,184	0,462	111	0,090	0,043	0,20
12	23,04	0,415	0,192	0,692	146	0,223	0,057	0,32
13	43,0	0,775	0,158	0,705	85	0,617	0,033	0,88
14	41,9	0,754	0,128	0,705	176	0,626	0,068	0,89

which lie within the limits of $0.325 \cdot 10^{-6}$ and $0.531 \cdot 10^{-6}$ [8], while for AU-10—AU-13, the constants B do not appreciably exceed $0.4 \cdot 10^{-6}$. Therefore, the differences in the values of W_0^c or v_{mi}^c , respectively, give the volumes of the micropores which are accessible to the smaller nitrogen molecules, but are not accessible to the larger benzene molecules [8]. In other words, they are a quantitative characteristic of the ultraporosity of the active carbons.

According to the data in the table, the limiting sorption volumes v_s for active carbons with respect to benzene are slightly greater than those with respect to nitrogen. For the samples studied, these differences lay within the range of 0.006–0.099 cc/g.

The reasons for this difference will be discussed in a separate communication. As a result, the volumes of the transitional pores of the active carbons calculated from experiments with benzene were 0.036–0.101 cc/g greater, for different samples, than the values determined from experiments with nitrogen. We used the averages of these values for analyzing the experimental data.

The conditions under which the isotherms for the adsorption of water vapor on AU-10—AU-14 were measured were the same as in the experiments described above, except that the sorption process was observed for longer periods. We did not arrive at this conclusion immediately and experiments with AU-10 and AU-11 occupied an intermediate position with respect to the duration of measurements of the increase in weight for each point on the adsorption isotherm. In experiments with subsequent samples of active carbons, in the regions of the sharp rise on the sorption branches of the isotherm, the duration of the observation of the increase in weight of a carbon sample for each point on the isotherm was 24 hr in the first series of experiments instead of 2–3 hr, but over the last 6–7 hr, no appreciable increase in weight was observed. In the final section of the isotherm close to $h = 1$, this time was increased to 2–3 days for each point on the isotherm.

Table 5 gives the results of experiments and calculations for limiting sorption ($h = 1$). For the corrected volumes of the micropores and transitional pores we used the mean values from experiments with benzene and nitrogen. The values of $v_s^{H_2O} - v_{mi}^c$ denote the volumes of water pertaining to the transitional pores under conditions where the volumes of the micropores are completely filled. They are comparable with the calculated volumes of the polymolecular adsorption layers v_t on the surfaces of the transitional pores at $h = 1$. The last column of the table gives the fraction of filling of the transitional pore volumes with liquid water at limiting sorption.

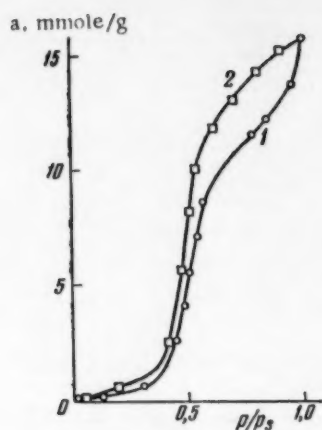


Fig. 1. Sorption (1) and desorption (2) isotherm for water vapor at 20° for active carbon P2.

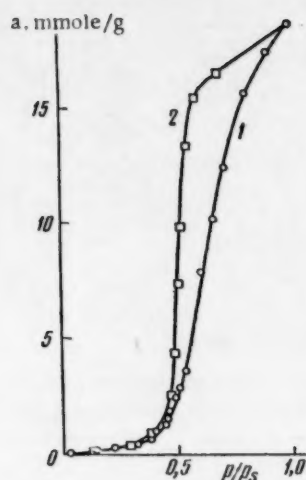


Fig. 2. Sorption (1) and desorption (2) isotherm for water vapor at 20° for active carbon G4.

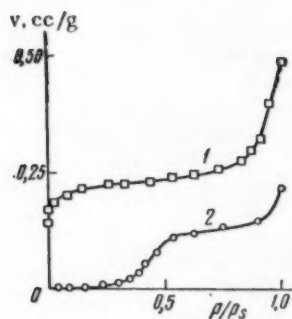


Fig. 3. Sorption branches of isotherms for the sorption of nitrogen at -195° (1) and water vapor at 20° (2) on AU-10.

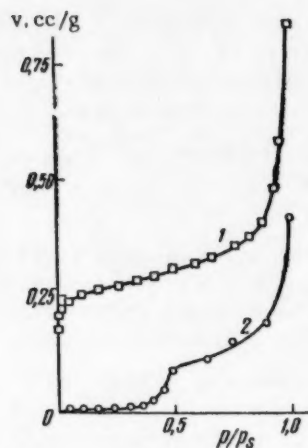


Fig. 4. Sorption branches of isotherms for the sorption of nitrogen at -195° (1) and water vapor at 20° (2) on AU-12.

According to the data in Table 5, for the first two samples of carbon, AU-10 and AU-11, the volumes of water sorbed in the transitional pores differ inappreciably from the volumes of polymolecular adsorption layers on the surfaces of the transitional pores, i.e., confirm the results of the first series of experiments. The increase in the time over which the increase in weight of the carbon samples was observed for the points on the isotherms of the next carbon samples, AU-12-AU-14, led to considerable filling of the transitional pores that greatly exceeded the volumes of polymolecular adsorption layers which could be formed at limiting sorption on the surfaces of this variety of pore. It is evident that despite the considerable increase in the duration of the experiments, we

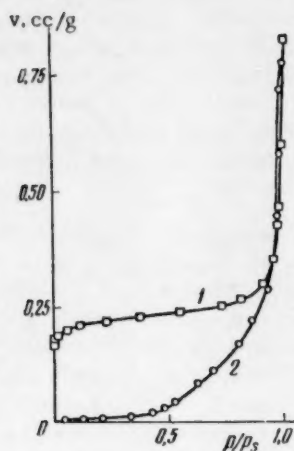


Fig. 5. Sorption branches of isotherms for the sorption of nitrogen at -195° (1) and water vapor at 20° (2) on AU-13.

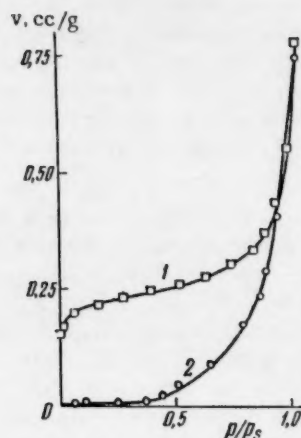


Fig. 6. Sorption branches of isotherms for the sorption of nitrogen at -195° (1) and water vapor at 20° (2) on AU-14.

had still not reached the equilibrium state in the region of high relative pressures. Therefore, it can be considered that there is a real possibility of complete filling of the volumes of transitional pores with liquid water at limiting sorption if the experiment times are increased even more. Consequently we can report the extremely low rates of sorption of water vapor in the region of high relative pressures for active carbons with a developed transitional porosity.

Figures 3-6 show sorption branches of isotherms for the sorption of nitrogen at -195° and water vapor at 20° for typical active carbon samples. For convenience in comparison, the sorption volumes V in cc/g, giving the volumes of sorbed substances, in the liquid state, are plotted along the ordinate axes of the graphs. In calculating them, we used tabular values of the densities of the corresponding liquids. The form of the sorption isotherms for water vapor on AU-10, AU-11, and AU-12 is of the first type and that of the sorption isotherms for AU-13 and AU-14 is of the second type.

From Fig. 3, it follows that for AU-10 the sorption of water vapor mainly leads to filling of the volume of the carbon micropores. In the case of AU-12 (Fig. 4), there is considerable filling of the volumes of the transitional pores. For carbons AU-13 and AU-14 (Figs. 5 and 6) there is filling of almost the whole of the sorption volume, i.e., the micropores and transitional pores of the active carbons. In the case of these carbons, the filling of the micropore volumes is complete at relative pressures of 0.80-0.85; the volume of the transitional pores is filled at an extremely low rate at higher pressures in the range 0.80-1.0.

DISCUSSION OF EXPERIMENTAL RESULTS

On the basis of experimental data, as a result of limiting sorption of water vapor with comparatively short measurement times for each point on the isotherm (up to 3 hr), there is filling of the volumes of active carbon micropores, and polymolecular adsorption layers are formed on the surface of transitional pores (Table 3). The good agreement between the volumes of the sorbed water and the volumes of the micropores found from experiments with benzene indicates that the density of sorbed water in the micropores is very close to the density of the liquid in the bulk phase if tabular values of the density are used for benzene.

In longer experiments at relative pressures of $h = 0.80-0.85$, filling of the volumes of the transitional pores begins for AU-13 and AU-14 and this is probably due to capillary condensation. Assuming that there is complete wetting and an equilibrium state, according to Kelvin's formula, these relative pressures correspond to effective pore radii of 48 and 65 Å, respectively, which are typical of transitional pores in order of magnitude.

It is well-known that for hydrophilic adsorbents, for example, mono disperse silica gels with predominant effective pore radii of 45 to 100 Å, the kinetics of capillary condensation of water vapor are the same as the kinetics observed for condensation of nitrogen, alcohol, and hydrocarbon vapors. Thus, according to our experiments, the limiting sorption volumes for water on finely and coarsely porous silica gels do not differ essentially from the limiting sorption volumes of nitrogen, cyclohexane, and benzene [12]. Neither did we observe any appreciable difference in the kinetics of water and hydrocarbon vapor sorption in the region of high equilibrium pressures. Thus, the low rate of capillary condensation of water vapor in transitional pores of active carbons is not due to the pore dimensions.

The most probable explanation of the low rate of capillary condensation of water vapor is connected with the more hydrophobic nature of the surface of active carbon and the peculiarity of the structure of a statistical polymolecular adsorption layer in the region of high relative pressures. Thus, at $h = 1$, the limiting sorption of water vapor per unit surface of black $A_s = 2.14 \cdot 10^{-2}$ mmole/m². If it is assumed that the monomolecular area for water $\omega = 13$ Å, then the adsorption layer on a black consists of only 1.7 statistical monolayers even when $h = 1$. In the light of ideas on the mechanism of water vapor adsorption [3], one can hardly expect the formation of a close-packed adsorption layer, especially at lower relative pressures; the layer apparently consists of separate islands lying at the primary adsorption centers -- chemisorbed oxygen molecules [5]. In this case, the lack of wetting of the surface of active carbon pores by water may be an obstacle to capillary condensation in transitional pores of active carbon. During the adsorption of water vapor in micropores, the small component of the dispersion interaction may promote the filling of the volume of the micropores at relatively high pressures (up to $h = 0.80 - 0.85$ in experiments with AU-13 and AU-14).

It is known that at 25°, liquid water slowly reacts with the surface of active carbon to form surface oxygen complexes (surface oxides) of carbon [13]. In this case, the increase in the number of adsorption centers may lead to merging of the "islands" and the formation of an adsorption layer sufficient for wetting ($\cos \theta > 0$). The result would be capillary condensation of water vapor in the transitional pores and then the kinetics of capillary condensation would determine the rate of the slow formation of additional primary adsorption centers.

A possible indirect confirmation of the increase in the number of primary adsorption centers [3] is the position of the desorption branches of the sorption isotherms for the active carbon samples studied. In the initial regions of the isotherms, the desorption branches lie above the sorption branches and the range of relative pressures corresponding to their sharp rise lies at lower pressures. In the next development of the investigations we will attempt to make a direct experimental proof of the working hypothesis formulated.

SUMMARY

1. Isotherms for the sorption of water vapor by active carbons with a developed transitional porosity have been studied.
2. Under measurement conditions corresponding to the attainment of sorption equilibrium for organic vapors, at the limiting sorption of water vapor by active carbons there is filling of the volumes of micropores with liquid vapor and the formation of a polymolecular adsorption layer on the surface of transitional pores.
3. In much longer experiments, there was filling of the volume of transitional pores of active carbons as a result of capillary condensation of water vapor.
4. The possible reasons for slow capillary condensation of water vapor in transitional pores of active carbon are discussed.

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ROLE OF THE SURFACE
IN THE MACROSCOPIC STAGES
OF ISOBUTANE OXIDATION
IN THE PRESENCE OF HBr

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In our previous work [1-4] it was shown that the mechanism of isobutane oxidation in the presence of HBr includes two clearly expressed macroscopic stages, separate in time. The first stage is the oxidation of isobutane by oxygen with the formation of tert-butyl hydroperoxide; the second does not involve molecular oxygen and is a complex decomposition of the hydroperoxide and its reaction with the original hydrocarbon.

In the study of the kinetics of reactions with separate macroscopic stages, we made wide use of Koval'skii's proposed method of separative calorimetry [5]. A study of the heat evolution of the reaction mixture makes it possible to determine unequivocally whether the reaction contains macroscopic stages which are separate in time as this method provides a means of measuring directly the rate of heat evolution and consequently the rate of the reaction itself for each stage separately. From the absolute magnitude of heat evolution, it is possible to determine whether the reactions studied (macro stages) are homogeneous or heterogeneous, which gives very valuable information for constructing the mechanism of a complex oxidation process.

The application of separative calorimetry to the oxidation of isobutane in the presence of HBr made it possible for us to obtain in the present work yet another objective demonstration of the two-stage nature of this process and establish the role of the surface in the macroscopic stages of this reaction.

EXPERIMENTAL

The reaction was studied on a static vacuum apparatus. The reaction vessel, which was made of molybdenum glass, was washed with boric acid solution to stabilize the surface [6]. The differential thermocouple used for measuring heat evolution of the reaction mixture was made of one constantan and two copper wires, 0.05 mm in diameter in each case. The thermocouple was fitted inside fine quartz capillaries (0.44 mm in diameter), one of which lay in the center of the reaction vessel and the other at the wall of the vessel. The thermocouple junction for measuring the temperature in the central reaction zone was placed in the central capillary, while the junction for measuring the temperature at the wall was placed in the capillary on the vessel wall; both thermocouple junctions lay half way along the vessel. The thermoelectric current arising due to the difference in temperature of the reaction mixture at the center and walls of the vessel (ΔT) was measured with a mirror galvanometer with a sensitivity of $2.8 \cdot 10^{-9}$ a/mm/m.

It was expected that the application of this procedure to the oxidation of isobutane in the presence of HBr, as a result of the two-stage nature of the process, would make it possible to record two maxima of heat evolution from the reaction mixture: the first corresponding to the maximum rate of tert-butyl hydroperoxide formation and the second corresponding to the maximum rate of hydroperoxide decomposition and its reaction with isobutane.

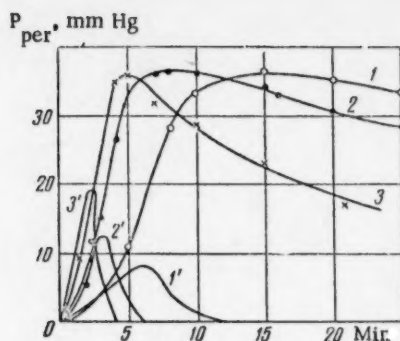


Fig. 1. Kinetic curves of tert-butyl hydroperoxide accumulation (1, 2, and 3) and curves of heat evolution by the reaction mixture (1', 2', and 3') at various temperatures. Mixture composition: 125 mm Hg $i\text{-C}_4\text{H}_{10}$ + 63 mm O_2 + 12 mm HBr. 1 and 1') $T = 170^\circ$; 2 and 2') $T = 180^\circ$; 3 and 3') $T = 190^\circ$.

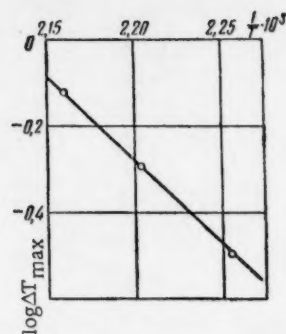


Fig. 2. Temperature dependence of maximum heat evolution (ΔT_{max}).

Figure 1 gives kinetic curves of tert-butyl hydroperoxide accumulation and of heat evolution by the reaction mixture in the oxidation of isobutane in the presence of HBr (125 mm Hg $i\text{-C}_4\text{H}_{10}$ + 63 mm O_2 + 12 mm HBr).

at various temperatures (170–190°). Fig. 1 clearly shows that, at all the temperatures studied, the heat-evolution maximum ΔT_{max} coincided in time with the point of inflection on the sigmoid kinetic curve of hydroperoxide accumulation, i.e., corresponded to the maximum rate of the first stage of isobutane oxidation in the presence of HBr. Beginning with the moment when the maximum hydroperoxide concentration was reached, the heat evolution of the reaction mixture became practically equal to zero. This result directly indicates that at the moment when the peroxide concentration reached a maximum peroxide formation ceased. Thus, the maximum concentration of peroxide is caused not by the fact that its rates of formation and consumption are equal, but by the fact that formation is practically completely replaced by hydroperoxide consumption.

The temperature dependence of ΔT_{max} is given in Fig. 2. The activation energy calculated from the slope of the lines equals 16.8 kcal/mole. This value agrees well with the value of 16.4 kcal/mole, obtained previously from kinetic curves of tert-butyl hydroperoxide accumulation. The agreement between these values indicates that the heat evolution actually completely reflects the rate of hydroperoxide formation and that this process is practically the sole reaction during the first macroscopic stage.

To determine the nature of the separate stages of isobutane oxidation, we made a special study of heat evolution of the reaction mixture with the surface of the reaction vessel and the central capillary treated in different ways. In work on propane oxidation catalyzed by hydrogen bromide [3] it was shown that covering the walls of the reaction vessel with a thin layer of KCl (by washing with KCl solution and subsequent drying) lead to complete suppression of reaction in this vessel. Therefore, in the present work we put a coating of KCl first on the surface of the reaction vessel (the central capillary was left clean) and then on the central capillary with the surface of the reaction vessel clean. In the first case, the isobutane was not oxidized at all and the galvanometer did not record any heat evolution by the reaction mixture. In the second case, when the central capillary was treated with KCl solution, there was normal oxidation of isobutane and the curve of the change in ΔT during the process coincided with the corresponding curve obtained before the KCl was deposited on the capillary surface. These experiments demonstrate directly that heat evolution by the reaction mixture, which corresponds to the rate of hydroperoxide formation, is caused by heat evolution in the volume of the reaction vessel and not on its surface. The role of the surface in this stage of the reaction is apparently heterogeneous chain termination.

The absence of heat evolution in the second stage of the process, despite the fact that the decomposition of tert-butyl hydroperoxide is accompanied by considerable heat evolution (78.9 kcal/mole, considering that tert-butyl hydroperoxide decomposes to acetone and methanol), is understandable only if it is assumed that the second stage of the reaction is heterogeneous. To check this hypothesis, we packed the reaction vessel with fine molybdenum glass tubes, which were washed with boric acid in the same way as the reaction vessel. This increased the ratio of the surface of the reaction vessel to its volume by a factor of 5. The kinetic curves of hydroperoxide

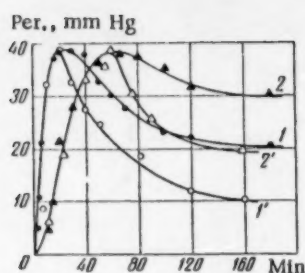


Fig. 3. Kinetic curves of hydroperoxide accumulation in an empty vessel (1 and 2) and in a vessel with a packing (1' and 2'). 1 and 1') $T = 170^\circ$; 2 and 2') $T = 150^\circ$.

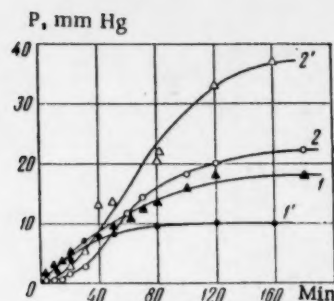


Fig. 4. Kinetic curves for the accumulation of tert-butanol (1 and 1') and acetone (2 and 2') in the oxidation of isobutane in the presence of HBr. $T = 170^\circ$; 1 and 2) in an empty vessel; 1' and 2') in a packed vessel.

accumulation in a vessel with a packing (Fig. 3) clearly demonstrate the different action of the packing on the first and second stages of the reaction and thus confirm our hypothesis on the different nature of these stages.

The accumulation of hydroperoxide in an empty vessel (curves 1 and 2) and in a vessel with a packing (curves 1' and 2') proceeds completely identically: the kinetic curves coincide. At the same time, in a vessel with a packing there is considerable acceleration of hydroperoxide consumption, i.e., there is a clear effect of surface on the second macroscopic stage. Fig. 3 gives two such series of experiments at 150 and 170° . The effect of the packing was the same at the two temperatures. As we have reported previously [2], there was the very interesting effect of a constant maximum concentration of hydroperoxide in the oxidation of isobutane in the presence of HBr at different temperatures. There was no change in the maximum hydroperoxide concentration with a change in the reaction vessel surface. In both cases, the consumption of hydroperoxide began only after this maximum hydroperoxide concentration had been reached. Thus, we have here two macroscopic stages that are clearly separate in time.

The lack of an effect of the packing on the kinetics of the process in the first stage is a direct demonstration of the homogeneous character of tert-butyl hydroperoxide, which occurs during this stage with heterogeneous chain termination. The acceleration of the second stage with an increase in the vessel surface indicates the heterogeneous nature of this stage.

As was established previously, the consumption of tert-butyl hydroperoxide in the oxidation of isobutane in the presence of HBr proceeds in two directions, namely, decomposition of hydroperoxide with the formation of acetone and reaction of hydroperoxide with isobutane to form tert-butanol. We were able to detect a change in the kinetics of acetone and alcohol accumulation when the reaction vessel was filled with a glass packing (Fig. 4). As Fig. 4 shows, in the presence of the packing there was a considerable increase in the amount of acetone formed and a decrease in the amount of butanol. This indicates that the introduction of packing accelerates hydroperoxide decomposition.

DISCUSSION OF RESULTS

All the conclusions we have drawn on the role of the surface in the two macroscopic stages may be confirmed by evaluations of the heat evolution of the reaction mixture by known formulas. If there is a reaction in a gas involving evolution of heat which is distributed uniformly through the volume of the reaction vessel, i.e., there is a purely homogeneous reaction, then for a cylindrical reaction vessel the heating in the center of the vessel is given by

$$\Delta T_{\max} = \frac{q_1}{4\lambda} R^2, \quad (1)$$

where q_1 is the amount of heat liberated per second per cc of mixture as a result of the chemical reaction, λ is the thermal conductivity coefficient, and R is the radius of the vessel.

The rate of heat evolution q_1 equals the product of the reaction rate and its heat effect. If the rate of the chemical reaction is expressed in millimeters of mercury per second at the experiment temperature (T_1), then we obtain the following expression for ΔT_{\max} :

$$\Delta T_{\max} = \frac{Q \cdot W \cdot R^2}{4 \cdot 760 \cdot 22400 \lambda} \cdot \frac{237}{T_1} \quad (2)$$

If the heat effect of the reaction is known and its rate is determined by an independent method, then from formula (2) we may obtain the heating for a homogeneous process.

If the heat-evolution conditions correspond to a purely heterogeneous process, i.e., if heat evolution occurs only at the surface of the reaction vessel and, consequently, on the surface of the central capillary which is made of the same material as the reaction vessel, then for a cylindrical vessel in this case we obtain:

$$\Delta T_{\max} = \frac{q_2}{4\pi\lambda} \cdot \frac{2r}{R+r} \cdot \ln \frac{R}{r} \quad (3)$$

where q_2 is the amount of heat liberated per unit time per unit length of the reaction vessel and r is the radius of the central capillary.

In the first stage of isobutane oxidation in the presence of HBr, the main reaction product is tert-butyl hydroperoxide. The heat effect of its formation is 21,000 kcal/mole. The vessel radius $R = 1.5$ cm and λ was taken to equal $8 \cdot 10^{-5}$ cal/cm·sec·deg. By substituting these values and also the reaction rate obtained from the curve of hydroperoxide accumulation at 180° (Fig. 1, curve 2), $w = 0.13 \pm 0.005$ mm Hg/sec in equation (2), we obtain the heating in the center of the vessel for a completely homogeneous reaction as equal to $\sim 0.6^\circ$. The value of ΔT_{\max} obtained experimentally at this temperature was 0.5° . If we assumed that the formation of tert-butyl hydroperoxide was heterogeneous, then the heating during the first stage of the reaction calculated from formula (3) would be only 0.1° at an oxidation temperature of 180°. Thus, a comparison of the heating values obtained experimentally with the values calculated for a homogeneous or heterogeneous reaction indicates that the first macroscopic stage of this process, i.e., the formation of tert-butyl hydroperoxide, is homogeneous.

No heating of the reaction mixture was observed during the second stage of the reaction. This fact and also the results of experiments with the reaction vessel filled with a glass packing indicate that the second stage of the reaction is heterogeneous. The same conclusion is reached by comparing the experimental value of maximum heating of the reaction mixture with the corresponding value calculated for a homogeneous second stage. This comparison is particularly interesting in connection with the fact that the reaction rate in the second stage is considerably less than the rate of hydroperoxide formation (see Fig. 1) and, consequently, if the second stage were homogeneous, the heating might be so small that it would lie below the sensitivity of the galvanometer used. Calculation by formula (2) gave a value for homogeneous heating for the second stage of the reaction at 180° equal to 0.17° . This value is only a factor of ~ 5 less than the heating observed in the first stage and undoubtedly would have been recorded by the galvanometer had the second stage been homogeneous.

Thus, a quantitative study of heat-evolution conditions in isobutane oxidation in the presence of HBr confirms the qualitative appraisal of this process, namely, that the first macroscopic stage of the process is homogeneous, while the second stage is heterogeneous.

SUMMARY

1. By separative calorimetry we confirmed that isobutane oxidation in the presence of HBr has two macroscopic stages that are separate in time.
2. It was established that the first stage, which is the formation of tert-butyl hydroperoxide, is homogeneous, while the second stage, which is decomposition of tert-butyl hydroperoxide and its reaction with isobutane, is heterogeneous.

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TWO MECHANISMS OF CARBON FORMATION
IN THE DECOMPOSITION OF n-PARAFFINS,
NAPHTHENES, AND AROMATIC HYDROCARBONS
WITH SIX AND SEVEN CARBON ATOMS
ON SILICA GEL

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The existence of differences in the pyrolysis of some hydrocarbons at comparatively low and high temperatures has been reported previously by a number of authors [1-3]. We showed [4, 5] that the difference in the pyrolysis of benzene homologs on silica gel at different temperatures is expressed most clearly in carbon formation. Two carbon-formation mechanisms (low-temperature up to 660-745° and high-temperature above 745-785°) are observed in the decomposition of benzene homologs; in the case of benzene itself, there is only one mechanism over the same temperature range.

The change in mechanism appears as a check in carbon formation in the temperature range 660-785° at 7-9% conversion of the original hydrocarbon into carbon and as a new increase in carbon-formation rate with a further rise in temperature. The low-temperature mechanism may be represented as a multistage dehydrocondensation with a complete use of the carbon of the starting materials, while the high-temperature mechanism is dehydrocondensation of benzene nuclei with preliminary dealkylation of starting alkylbenzenes. With the low-temperature mechanism, the condensation proceeds mainly through the alkyl groups; with the high-temperature mechanism, it proceeds through the nuclei. The change in mechanism is caused by the development of destructive hydrogenation of the starting hydrocarbons or their dehydrocondensation products by the hydrogen liberated in carbon formation. In the present investigation we attempted to determine whether there is a difference in the carbon-formation mechanism at different temperatures in the decomposition of other hydrocarbons, in particular, cyclohexane, methylcyclohexane, n-hexane, and n-heptane in comparison with benzene and toluene.

EXPERIMENTAL

The experiments were carried out by the same procedure as in the previous investigation [5], i.e., in a quartz reactor of a flow, heterogeneous catalytic apparatus with an indirect-temperature regulation system [4, 6, 7], over the temperature range 500-900° at atmospheric pressure. The same silica gel of KSM grade with a grain size of 1-2 mm was used as a catalyst. A fresh portion (5 ml) of catalyst was used for each experiment. The reagents (Table 1) were introduced at the same rate of 4.78 ml/hr. Each experiment lasted for 2 hr. The apparatus was flushed with nitrogen before and after an experiment. The carbon was determined with an accuracy of up to 0.0001 g by direct weighing; the tarry condensation products were determined by analysis of the quantitatively-collected catalyzate with an accuracy of 1% of the value determined. The gaseous products were determined by means of a Patrikeev automatic gasometer (UGSP) and subjected to analysis on a BTI apparatus and low-temperature rectification on a TsLATIM-51u apparatus. The liquid part of the catalyzate was distilled on a fractionating column with an efficiency of 30 theoretical plates and the substances obtained were identified.

TABLE 1

Constants of Starting Hydrocarbons

Starting hydrocarbon	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}
Benzene	79,1 (743)	0,8790	1,5013
Toluene	109,2 (748)	0,8669	1,4965
Cyclohexane	78,6—78,8 (750)	0,7811	1,4272
Methylcyclohexane	99,2—100,4 (761)	0,7695	1,4234
n-Hexane	68,1—68,5 (750)	0,6599	1,3751
n-Heptane	96,6—98,0 (744)	0,6836	1,3879

The characteristics of benzene and toluene decomposition on silica gel will not be discussed here as special attention was devoted to them in our previous communication [5]. In the present discussion, we will present only data on the behavior of these hydrocarbons which is necessary for comparison with the naphthenes and paraffins investigated in this work.

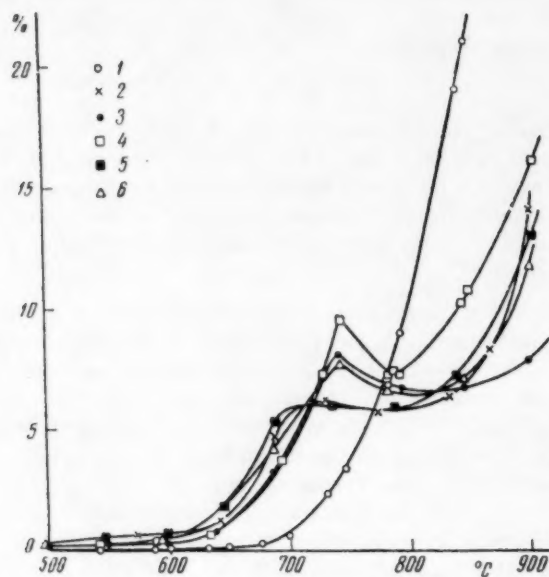


Fig. 1. Temperature dependence of carbon formation (conversion of hydrocarbon introduced into carbon in %) during the decomposition of benzene (1), cyclohexane (2), n-hexane (3), toluene (4), methylcyclohexane (5), and n-heptane (6) on silica gel.

As Fig. 1 shows, the increase in the rate of carbon formation with a rise in temperature in the case of cyclohexane, methylcyclohexane, n-hexane, and n-heptane shows a check in the temperature range 690–825° which is specific for each of the hydrocarbons. The check in carbon formation is analogous to the phenomenon for toluene and lies in approximately the same temperature range as for toluene and other benzene homologs. Evidently, the reason for the given check in carbon formation in the case of the naphthenes and paraffins investigated is also a change in the carbon-formation mechanism, as in the case of alkylbenzenes.

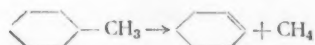
TABLE 2

Analysis Results for Contact Gases

Starting hydrocarbon	Experiment temperature in °C	Composition of contact gases in vol. %		
		hydro-gen	unsatur-ateds	satur-ateds
Cyclohexane	690	59	22	19
	735	47	24	29
	870	41	8,5	51
n-Hexane	598	4	55	41
	741	7	41	52
	793	11	30	59
Methylcyclohexane	593	32	49	19
	738	46	25	29
	904	72	6	22
n-Heptane	594	5	78	18
	743	7	45	48
	845	8	26	66

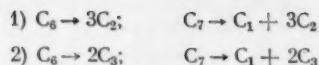
A comparison of the analysis results for the contact gases (Table 2) shows that the amount of unsaturated hydrocarbons in the gas decreased with a rise in temperature and this was particularly sharp at temperature above 750°, while the amount of saturated hydrocarbons increased. The coincidence of the temperature ranges of the check in carbon formation and the sharp reduction in the amount of unsaturated hydrocarbons indicates that there is a connection between these phenomena. Apparently, the low-temperature carbon-formation mechanism in the case of the two naphthenes and paraffins indicated has as its first stage the formation of unsaturated hydrocarbons from the starting hydrocarbons and is a polycondensation of these unsaturated hydrocarbons. The higher rates of carbon formation from cyclohexane and methylcyclohexane at low temperatures in comparison with n-hexane and n-heptane (see Fig. 1) apparently may be explained by the fact that the starting material for carbon formation in this case is cyclohexene, together with ethylene and propylene, which is the only starting material in the case of n-hexane and n-heptane. This is confirmed by the results of rectifying the liquid part of the catalyzate. For low-temperature experiments with cyclohexane and methylcyclohexane, we found up to 7% of an unsaturated fraction with b.p. 82°, n_D^{20} 1.4450, which was evidently cyclohexene. At the same time, we did not detect unsaturated hydrocarbons in the liquid part of the catalyzate from experiments with n-hexane and n-heptane.

The conclusion that the starting hydrocarbons are converted into olefins in the first stage of low-temperature carbon formation agrees with the observations of Andreev and Klimenok et al., [8, 9], who showed that in the cracking of paraffins on an aluminosilicate catalyst at 520°, the carbon is formed as a result of the polymerization of olefins, and also with the data of other authors, who reported that olefins play an essential part in coke formation [10-13]. In low-temperature carbon formation, the olefins are formed by cracking of the starting hydrocarbons. Judging by the composition of the hydrocarbon gases (Table 3), cyclohexane and n-hexane give only C₂ and C₃ hydrocarbons on cracking,* while methylcyclohexane and n-heptane give considerable amounts of methane in addition to C₂ and C₃ hydrocarbons. In addition, cyclohexene is formed in the dehydrogenation of cyclohexane and the cracking of methylcyclohexane, which probably proceeds according to the scheme:



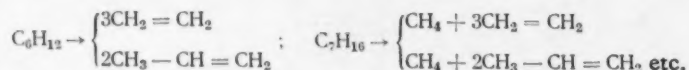
Judging by the composition of the gases, the two following schemes are equally probable in the cleavage of cyclohexane and methylcyclohexane molecules:

*This conclusion agrees with the data of Jost and Muffling [14], who showed that the hydrocarbon gases consist solely of C₂ and C₃ hydrocarbons in the cracking of cyclohexane.

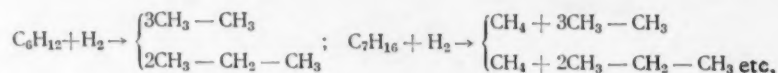


In the case of n-hexane and n-heptane, the probability of the first scheme is greater than that of the second in the ratio 3/5:2/5.

A comparison of the data in Tables 2 and 3 indicates that together with the cracking reactions:



there are also destructive hydrogenation reactions:



as the gases contain more saturated hydrocarbons than is required according to the cracking scheme.

TABLE 3

Results of Fractionating Contact Gases on a TsIATIM-51u Apparatus

Starting hydrocarbon	Temp. (°C)	Fraction in vol. %			
		methane	ethane-ethylene	propane-propylene	butane-butylene
Cyclohexane	743	0	49	51	0
n-Hexane	750	5	60	35	0
Methylcyclohexane	740	42	29	29	0
n-Heptane	741	45	34	21	0

Consequently, the reason for the check in carbon formation in the temperature range 690-825° may be regarded as suppression of the cracking reactions, which give the starting material for carbon formation, by destructive hydrogenation reactions. The hydrogen required for destructive hydrogenation is liberated during the carbon formation itself. The hydrogen concentration in the reaction sphere reaches a considerable value (partial pressure ~300 mm Hg) at 6-8% conversion of the starting hydrocarbon into carbon when there is the check in carbon formation. The relative amounts of hydrogen at this moment have the following values for the hydrocarbons studied if the value for toluene is taken as unity: cyclohexane 1, methylcyclohexane 1.2, n-hexane 1.6, and n-heptane 1.7. From this it follows that hydrogenolysis of the methyl group of toluene and rupture of the cyclohexane ring proceed with approximately the same ease; the hydrogenolysis of normal paraffins proceeds with much greater difficulty.

The new increase in carbon-formation rate with a further rise in temperature (see Fig. 1) is evidently connected with a change in carbon-formation mechanism, whereby the preliminary formation of olefins becomes unnecessary, i.e., the starting materials for carbon formation are some other substances. Apparently, the high-temperature carbon-formation mechanism in the decomposition of the four given substances is successive dehydrocondensation of saturated hydrocarbons (both the starting hydrocarbons and their hydrogenolysis products) with the carbon material, leading to the gradual build up of its polycyclic structures. Another possible route in high-temperature carbon-formation is multistage dehydrocondensation of benzene and other aromatic hydrocarbons, which are first formed from the starting materials. It is most probable that both directions occur and with an increase in temperature and hydrogen concentration, the second direction is increasingly replaced by the first.

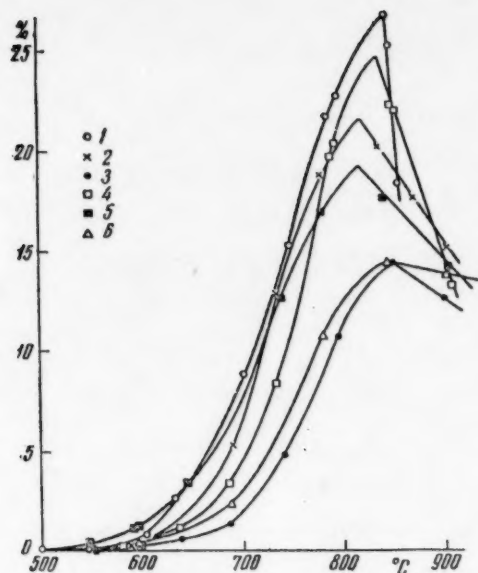


Fig. 2. Temperature relation of the formation of volatile tarry condensation products (conversion of hydrocarbon introduced in %) during the decomposition of benzene (1), cyclohexane (2), n-hexane (3), toluene (4), methylcyclohexane (5), and n-heptane (6) on silica gel.

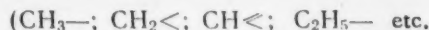
each of the pairs of substances with the exception of methane (see Table 3), which, apparently, is not a starting material for carbon formation in the temperature range investigated. Likewise, the results obtained cannot be explained by assuming the preliminary formation of complex radicals ($\text{C}_6\text{H}_5\text{—}$; $\text{C}_6\text{H}_4\text{—CH}_2\text{—}$; $\text{C}_6\text{H}_3\text{—}$; $\text{C}_6\text{H}_2\text{—}$ etc.) as in this case there should be appreciable differences in the behavior of cyclohexane and methylcyclohexane, n-hexane and n-heptane, which is not the case.

The possibility of high-temperature carbon formation by multistage dehydrocondensation of aromatic compounds, which are first formed from the starting materials and their conversion products, is confirmed by the presence of aromatic hydrocarbons in the liquid and tarry parts of the catalyzate, which we observed. This agrees completely with the observations of a number of authors [15-22], who reported the formation of aromatic substances when the hydrocarbons we studied were passed over aluminosilicate and other nonmetallic catalysts.

As follows from Fig. 2, the rates of formation of volatile tarry condensation products for all the substances investigated show maxima in the temperature region 815-845°, while there are no checks in the formation of these compounds in the region where the carbon-formation mechanism changes. Thus, carbon formation and the formation of volatile tarry condensation products are, to a certain extent, independent processes. As in the case of alkylbenzenes [5], this may be explained by the fact that volatile tarry condensation products, which are aromatic compounds with molecular weights 2, 3, 4, etc. times greater than the starting hydrocarbons, do not play a substantial role in carbon formation as a starting material and that the main increase in carbon occurs as a result of polycondensation of the starting hydrocarbons and their simplest conversion products with the carbon material.

The individual nature of each hydrocarbon is reflected in the rates of formation of volatile condensation products, as is shown by a comparison of the curves in Fig. 2 and the data in Table 4. Benzene shows the greatest rates of formation of volatile condensation products and paraffins, the lowest. The substances may be arranged in the following series according to the rates of formation of these products:

In the given case, it is not necessary to assume that a substantial role is played by free aliphatic radicals in the high-temperature carbon-formation mechanism. If there were preliminary formation of the simplest radicals



as the first stage of carbon formation, then there would not be differences in the course of carbon formation for different hydrocarbons due to the fact that the radical mixtures have practically the same compositions in different cases. Moreover, as follows from our observations in the case of alkylbenzenes [5] and in the present work, the nature of the hydrocarbon is reflected in the specific course of carbon formation both in the low- and high-temperature mechanisms. There are sharp differences in the course of carbon formation for benzene, toluene, hydroaromatic hydrocarbons, and normal paraffins. The hydrocarbons of one class, cyclohexane and methylcyclohexane or n-hexane and n-heptane, hardly differ among themselves as the carbon-formation curves practically coincide, while there are clear differences in the different classes and also between benzene and toluene (see Fig. 1). The lack of differences in the behavior of cyclohexane and methylcyclohexane, on the one hand, and n-hexane and n-heptane, on the other, likewise does not support the adoption of a radical scheme with an intermediate formation of the simplest radicals. These characteristics are completely explained by the identical composition of the starting material for carbon formation in

TABLE 4

Maximum Degrees of Conversion of Hydrocarbons into Volatile Tarry Condensation Products

Hydrocarbon	Maximum conversion of substance introduced in %	Temperature of maximum in °C	Hydrocarbon	Maximum conversion of substance introduced in %	Temperature of maximum in °C
Benzene	27	845	Methylcyclohexane	19	815
Toluene	24	825	n-Hexane	14	845
Cyclohexane	22	815	n-Heptane	14	845

Benzene > cyclohexane > n-hexane
 v
 Toluene > methylcyclohexane > n-heptane

Approximately the same order is observed in the rates of high-temperature carbon formation.

This order in the rates of formation of condensation products, which are various aromatic and polycyclic systems, may be explained by the fact that in the case of benzene and toluene there are existing aromatic nuclei, which condense; in the case of hydroaromatic hydrocarbons and paraffins preliminary aromatization of the substance is necessary and this is most difficult for paraffins. Data on the rates of evolution of contact gases in each case (Fig. 3) are in agreement with this explanation. The rates of gas formation increase sharply from benzene and toluene to n-heptane and an analogous picture is observed in the case of benzene, cyclohexane and n-hexane. This indicates that the formation of condensed products is more difficult the greater the amount of volatile by-products accompanying this process.

SUMMARY

1. A study was made of the pyrolysis of cyclohexane, methylcyclohexane, n-hexane, and n-heptane, in comparison with benzene and toluene, over the range 500-900° on silica gel. It was confirmed that in this case there are two different carbon-formation mechanisms: a low-temperature one up to 690-745° and a high-temperature one at temperatures above 785-825°, which have their own peculiarities for each of the hydrocarbons.

2. In all the cases studied, carbon formation consists of polycondensation of either the starting hydrocarbons or some of their preliminary conversion products.

3. Carbon formation occurs mainly as a result of polycondensation of the starting material for carbon formation with the carbon material. Free aliphatic radicals are of no great importance as starting materials for carbon formation.

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Fig. 3. Temperature dependence of the rate of evolution of contact gases in the decomposition of benzene (1), toluene (2), methylcyclohexane (3), and n-heptane (4) on silica gel.

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KINETICS AND MECHANISM OF THE REACTION OF ETHYL RADICALS WITH MOLECULAR OXYGEN

COMMUNICATION 2. DEPENDENCE OF REACTION KINETICS

ON THIRD PARTICLE

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In the first part [1] of the present work we presented a method and the results of measuring the rate constants of recombination of ethyl radicals and the rate constant of the reaction of ethyl radicals with molecular oxygen with a constant concentration of the third particle. In the present article we present results of an investigation with different concentrations of the third particle.

To determine the role of the third particle in the recombination of ethyl radicals and their reaction with oxygen molecules, it is necessary to know the pressure dependence of both the sum $k_0 + k_0''$ ($C_2H_5)_0$ and the value k_1 or $k_2(M)$ or the sum $k = k_1 + k_2(M)$. For this purpose, we used the method described previously [1] to carry out several series of experiments at different pressures from 2 to 11.5 mm. The results of these experiments are given in Fig. 1,

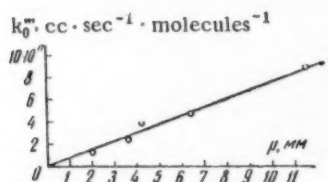
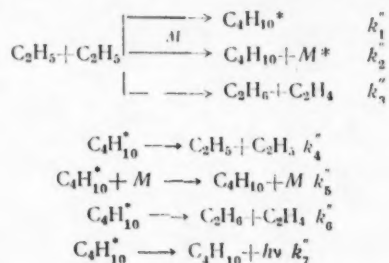


Fig. 1. Experimental pressure dependence of the effective rate constant of ethyl radical destruction.

where the pressure in millimeters of mercury is plotted along the abscissa axis and the value of k_0'' along the ordinate. Fig. 1 shows that over the pressure range investigated, the constant of quadratic destruction k_0'' is proportional to pressure.

To understand the relation of k_0'' to pressure, let us examine the mechanism of quadratic recombination of ethyl radicals. If we consider the following processes and adopt the most general scheme



where k_1'' , k_2'' , etc., are the rate constants of the corresponding elementary reactions, $C_4H_{10}^*$ is a butane molecule rich in energy, and M is the third particle, then from the condition for the stationary state

$$\frac{d(C_4H_{10}^*)}{dt} = 0 \tag{1}$$

we obtain

$$k_1''(\text{C}_2\text{H}_5)^2 = (\text{C}_4\text{H}_{10}) (k_4'' + k_5''M + k_6'' + k_7''). \quad (2)$$

For the total rate of disappearance of C_2H_5 radical, according to the scheme, it is correct to write

$$\frac{d(\text{C}_2\text{H}_5)}{dt} = -2k_5(\text{C}_2\text{H}_5)^2 + 2k_4'(\text{C}_4\text{H}_{10}), \quad (3)$$

where

$$k_5 = k_1'' + k_2''M + k_3''.$$

By substituting the value of C_4H_{10} from (2), we obtain

$$\frac{d(\text{C}_2\text{H}_5)}{dt} = -k_0'''(\text{C}_2\text{H}_5)^2,$$

where

$$k_0''' = \frac{2k_1''(k_6'' + k_7'' + k_8''M)}{k_4'' + k_6'' + k_7'' + k_8''M} + 2k_3'' + 2k_2''M. \quad (4)$$

Formula (4) shows the structure and the pressure dependence of the effective constant of quadratic destruction of ethyl radicals when the destruction mechanism presented is adopted. The graphical representation of this function in the coordinates k_0''' and M depends on the ratio of the constants k_2'' ; k_4'' ; k_6'' and k_3'' . However, at any ratio of the constants, two types of graphs are possible: either a straight line or a curve tending to a limit. An examination of function (4) shows the following:

- 1) A straight line is obtained only when

$$k_2''M \gg k_1'' \left(\frac{k_6'' + k_7'' + k_8''M}{k_4'' + k_6'' + k_7'' + k_8''M} \right)$$

- 2) A curve with saturation is obtained with the condition:

$$k_2''M < k_1'' \left(\frac{k_6'' + k_7'' + k_8''M}{k_4'' + k_6'' + k_7'' + k_8''M} \right).$$

- 3) Both the line and the curve may pass through the origin of the coordinates and give an intercept on the ordinate axis.

- 4) Appreciable intercepts on the ordinate axis are obtained only when k_3'' is comparable with

$$\frac{k_1''(k_6'' + k_7'' + k_8''M)}{(k_4'' + k_6'' + k_7'' + k_8''M)}$$

or if $k_6'' + k_7''$ is comparable with and greater than $k_8''M$.

Figure 2 shows various forms of the function $k_0''' = f(M)$, calculated from formula (4) for various ratios of the constants. The concentration of the third particle (M) is expressed here as the pressure p at $T = 421^\circ\text{K}$. In

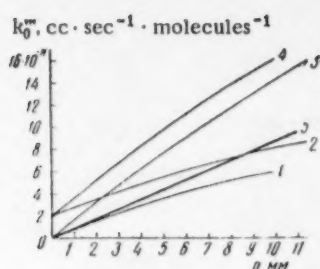


Fig. 2. Calculated possible cases of the pressure dependence of the effective rate constant of ethyl radical destruction: 1) Predominance of bimolecular recombination reactions; 2) predominance of bimolecular recombination with bimolecular disproportionation present; 3) termolecular reaction rate constant equal to bimolecular recombination constants; 4) the same as in 3, but with the presence of appreciable bimolecular disproportionation; 5) predominance of termolecular recombination.

Line 5 was obtained with the conditions

$$k_2''(M) \gg k_1'' \frac{k_6'' + k_7'' + k_8''M}{k_4'' + k_6'' + k_7'' + k_8''M} \text{ and } k_3'' \ll k_1''$$

A comparison of the experimental line (Fig. 1) with various forms of the curve calculated from formula (4) (Fig. 2) shows that the experimental line is close to the calculated line 5 in Fig. 2. In other words, it may be concluded that quadratic destruction of ethyl radicals mainly obeys a termolecular law with the constant k_2'' . Thus, the effective constant of quadratic destruction k_0'' may be expressed through the constant k_2'' if the first two terms are neglected in formula (4). Consequently

$$k_0'' = 2k_2''(M) \quad (5)$$

Equation (5) is the equation of the line presented in Fig. 1. Consequently, it is possible to obtain an approximate value for the constant k_2'' from the slope of the line in Fig. 1. In this way, from Fig. 1 we obtain:

$$k_2'' \approx 3 \cdot 10^{-28} \text{ cm}^6 \cdot \text{sec}^{-1}$$

This value of k_2'' was found for the case when the third particle is an H_2 molecule.

The conclusion that we reached on the predominance of the termolecular process determining the effective destruction of ethyl radicals is in good agreement with the experiments of other authors [2, 3], although Brinton and Steacie [2] reached a conclusion which does not agree with ours. Bradley, Melville, and Robb [3], who obtained

calculating all the curves, we used values of the constants k_1'' , k_4'' and k_5'' and ratios of them that were identical for all the curves, such that the calculated curves could be compared with experimental curves for the pressure range from 1 to 12 mm Hg which interested us.

Curve 1 was obtained with the conditions

$$k_2''(M) \ll k_1'' \frac{(k_6'' + k_7'' + k_8''M)}{(k_4'' + k_6'' + k_7'' + k_8''M)} \text{ and } k_3'' \approx k_2''(M)$$

Curve 2 was obtained with the conditions

$$k_2''(M) \ll k_1'' \frac{(k_6'' + k_7'' + k_8''M)}{(k_4'' + k_6'' + k_7'' + k_8''M)} \text{ and } k_3'' = 0, 1k_1''$$

Curve 3 was calculated with the conditions

$$k_2''(M) = k_1'' \frac{(k_6'' + k_7'' + k_8''M)}{(k_4'' + k_6'' + k_7'' + k_8''M)} \text{ and } k_3'' \ll k_2''(M)$$

Curve 4 was obtained with the conditions

$$k_2''(M) = k_1'' \frac{(k_6'' + k_7'' + k_8''M)}{(k_4'' + k_6'' + k_7'' + k_8''M)} \text{ and } k_3'' = 0, 1k_1''$$

C_2H_5 radicals by photolysis of diethylmercury with neon added over the range from 0 to 200 mm Hg, observed a clear increase in the butane : ethane ratio with an increase in the neon pressure. The authors explained this increase in the ratio by the pressure dependence of the rate constant of butane formation. Brinton and Steacie [2] investigated the effect of a third particle (diethyl ketone) on the recombination of ethyl radicals during the photolysis of diethyl ketone. These authors experimentally observed the pressure dependence of the butane : ethane ratio but explained this by the pressure dependence of the rate of ethane, and not butane, formation, assuming that the ethane was formed predominantly on the surface. If we adopt the other possible explanation for the rules observed in the experiments of Brinton and Steacie [2], namely, that butane formation proceeds by ternary collisions and its rate depends on the concentration of the third particle, while the rate of ethane formation is determined by a bimolecular volume process, which does not require a third particle, then the discrepancy in the conclusions disappears.

The quantitative aspects of the observations may also be put forward in support of the conclusion that termolecular recombination of ethyl radicals predominates in the pressure range from 2 to 11.5 mm. Let us assume that we were mistaken in taking the experimental line 1 to be a straight line and that in actual fact, it is not a straight line, but only the initial linear section of a curve, which does not reach a bend and saturation. In other words, let us assume that the termolecular process plays no part. In this case, the relation of k_0'' to pressure or M will be expressed not by formula (4), but by

$$k_0''' = 2k_1'' \frac{k_6'' + k_7'' + k_5''(M)}{k_1'' + k_6'' + k_7'' + k_5''(M)} \quad (6)$$

If we take reciprocals of the left-hand and right-hand parts of equation (6), then we obtain

$$\frac{1}{k_0'''} = \frac{1}{2k_1''} \left(1 + \frac{k_4''}{k_6'' + k_7'' + k_5''M} \right) \quad (7)$$

or if $k_6'' + k_7'' \ll k_5''M$, we obtain

$$\frac{1}{k_0'''} = \frac{1}{2k_1''} + \frac{k_4''}{2k_1''k_5''(M)} \quad (8)$$

Turning to the experimental data presented in Fig. 3, where the experimental values of $1/k_0'''$ and $1/p$ are plotted on the axes, we see that the graph is a straight line, indicating the accuracy of the inequality $k_6'' + k_7'' \ll k_5''M$. In addition the line does not intersect the ordinate axis, but passes through the origin of the coordinates. Therefore, we may write the inequality:

$$\frac{1}{2k_1''} < 0.01 \cdot 10^{11}$$

or

$$2k_1'' > 10^{-9}.$$

However, this inequality cannot be correct as any constant of a bimolecular process cannot be greater than $10^{-10} \text{ cc} \cdot \text{sec}^{-1}$. Consequently, the assumption that the termolecular process in the recombination of ethyl radicals may be neglected is contrary to quantitative experimental data. This quantitative evaluation of experimental measurements again indicates the predominance of the termolecular mechanism of ethyl radical recombination. It should also be noted, as follows from formula (4), at higher pressures the termolecular mechanism should predominate even more.

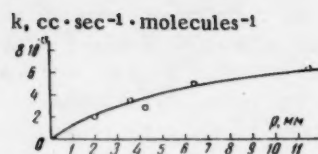
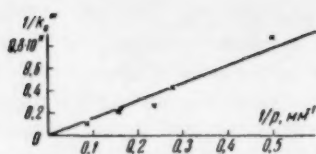
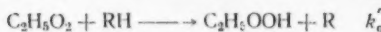
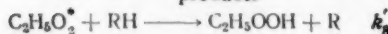
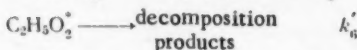
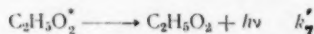
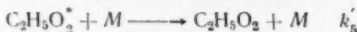
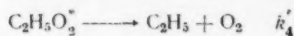
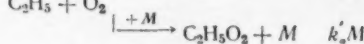
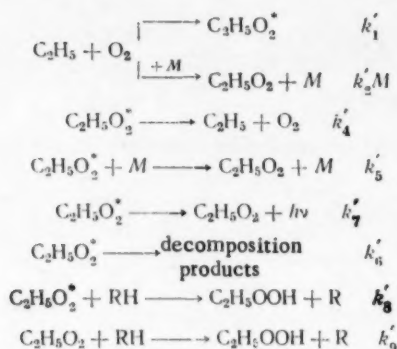


Figure 4 gives the pressure dependence of the effective rate constant k of the reaction of ethyl radicals with oxygen molecules. Fig. 4 shows that the reaction of an ethyl radical with an oxygen molecule over the pressure range studied involves a third particle. However, the value of k is not proportional to pressure over the whole pressure range. To determine the relation of k to pressure, let us examine the mechanism of the reaction of an ethyl radical with molecular oxygen. By considering all conceivable processes and adopting the most general scheme:



and using the conditions for the stationary state

$$\frac{d(C_2H_5O_2^*)}{dt} = 0,$$

we obtain

$$k'_1 (\text{C}_3\text{H}_5)(\text{O}_2) = (\text{C}_3\text{H}_5\text{O}_2^*) [k'_1 + k'_5 M + k'_7 + k'_6 + k'_8 (\text{RH})]$$

For the over-all rate for the interaction of C_2H_5 with O_2 , we obtain

$$\frac{\partial (C_2H_5)}{\partial t} = -k'_1 (C_2H_5) (O_2) - k'_2 M (C_2H_5) (O_2) + k'_4 (C_2H_5O_2^*) \quad (9)$$

By substituting the value of $C_2H_5O_2^*$, we obtain

$$-\frac{\partial (C_2H_5)}{\partial t} = k'_1 (C_2H_5) (O_2) + k'_2 M (C_2H_5) (O_2) - k'_1 \frac{k'_1 (C_2H_5) (O_2)}{k'_4 + k'_1 M + k'_2 + k'_6 + k'_8 (RH)}$$

Consequently, the effective rate constant for the reaction of an ethyl radical with an oxygen molecule k has the following structure:

$$k = k_2' M + \frac{k_1' [k_6' + k_7' + k_8'(\text{RH}) + k_5' M]}{k_4' + k_6' + k_7' + k_8'(\text{RH}) + k_5' M} \quad (10)$$

On comparing expression (10) with expression (4), which was obtained above, it is readily seen that these two expressions have the same type of pressure dependence. Therefore, a graphical representation of formula (10) is also given by Fig. 2. On comparing the experimental pressure dependence of the effective rate constant for the reaction of an ethyl radical with an O_2 molecule (Fig. 4) with the theoretical dependence derived from the general scheme of the reaction (Fig. 2), it is seen that over the pressure range investigated the bimolecular reaction with the constant k_1' predominates over the termolecular reaction with the constant k_2' . In addition to the effective constant k , which has already been measured, the experimental data obtained (Fig. 4) makes it possible to determine the value of the constant k_1' , which is the rate constant of the bimolecular process $\text{C}_2\text{H}_5 + \text{O}_2 \xrightarrow{k_1'} \text{C}_2\text{H}_5\text{O}_2^*$, and also the ratio of the rate constants k_4'/k_5' . In addition, these experimental data make it possible to estimate the upper limit of the constant k_2' .

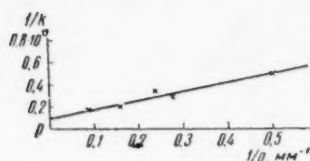


Fig. 5. Experimental relation of $1/k$ to $1/p_{\text{H}_2}$ for the reaction of ethyl radicals with oxygen molecules.

Figure 5, where $1/p$ is plotted along the abscissa axis and $1/k$ along the ordinate, gives a different form of the relation of the constant k to pressure p , which yields a straight line. In order to obtain an analytical expression for this relation, it is necessary to take reciprocals of the left-hand and right-hand parts of equation (10). Since a straight line is obtained experimentally, the equation must be a linear equation. Such an equation is obtained under the two following conditions:

- 1) $k_6' + k_7' + k_8'(\text{RH}) \ll k_5' M$
- 2) $k_2'(k_4' + k_5' M) \ll k_1' k_5'$.

Thus, we obtain

$$\frac{1}{k} = \frac{1}{k_1'} + \frac{k_4'}{k_1' k_5' M} \quad (11)$$

Consequently, the slope of the line in Fig. 5 gives the value of the product $k_4'/k_1'k_5'$. From the intercept on the ordinate we obtain the value k_1' and consequently, the value k_4'/k_5' . In this way we obtain the values $k_1' = 1.1 \cdot 10^{-12} \text{ cm}^3 \cdot \text{sec}^{-1}$ and $k_4'/k_5' = 2 \cdot 10^{-17} \text{ cm}^{-3}$. The ratio $k_4'/k_5' M$ is the ratio of the decomposition rate to the stabilization rate of the energy-rich peroxide radical. This ratio depends on the concentration of the third particle. When the third particle is a H_2 molecule, the ratio equals 8.65, 0.865, and 0.0865, when p equals 1, 10, and 100 mm Hg, respectively. Consequently, it may be stated that while from 90 to 50% of energy-rich $\text{C}_2\text{H}_5\text{O}_2^*$ radicals decompose at pressures from 1 to 10 mm, at $p_{\text{H}_2} = 100 \text{ mm}$, ~90% of these radicals are stabilized to normal peroxide radicals.

To estimate the upper limit of the constant k_2' from experimental data, we start from the following considerations: According to formula (10), the constant k is determined by two terms, one of which is $k_2' M$. As it was previously shown that under the conditions of our experiments at $M = 11.5 \text{ mm Hg}$, there is the condition $k \gg k_2' M$, then $k_2' \ll 2.3 \cdot 10^{-30} \text{ cm}^6 \cdot \text{sec}^{-1}$, since $k/M = 2.3 \cdot 10^{-30} \text{ cm}^6 \cdot \text{sec}^{-1}$.

SUMMARY

1. The pressure dependence of the rate constant of ethyl radical recombination was investigated. The recombination of ethyl radicals obeys the equation of termolecular reactions. The absolute values of the constants were determined.
2. The pressure dependence of the effective rate constant of the reaction of ethyl radicals with molecular oxygen was investigated over the range from 1 to 13 mm Hg.

3. We determined the rate constant (absolute) of the bimolecular formation of the energy-rich radical $C_2H_5O_2^*$ from a C_2H_5 radical and an O_2 molecule.

4. We found the upper limit of the termolecular rate constant for the formation of a normal $C_2H_5O_2$ radical from a C_2H_5 radical and a O_2 molecule for the case when the third particle is H_2 molecule.

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INVESTIGATION OF THE EFFECT OF
HYDROGEN PRESSURE ON THE RATE OF
HETEROGENEOUS CATALYTIC ISOMERIZATION
OF CYCLOHEXANE

COMMUNICATION 2. RELATION OF CYCLOHEXANE ISOMERIZATION RATE
TO PARTIAL HYDROGEN PRESSURE, TEMPERATURE, AND WS_2 GRAIN SIZE

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In our previous work [1] we presented the results of an investigation of the isomerization of cyclohexane to methylcyclopentane in the presence of tungsten sulfide in a flow system under a pressure of hydrogen. These results showed that the effect of hydrogen pressure on the cyclohexane isomerization rate depends on temperature. At 320 and 340°, an increase in the total pressure from 50 to 250 atm with constant cyclohexane and hydrogen input rates led to a decrease in the degree of isomerization; at 370°, the yields of reaction products changed insignificantly, but increased sharply with pressure at 400 and 430°. Over the temperature range 320-430°, the order of the reaction with respect to cyclohexane was found to equal 0.4. At 430°, the reaction rate constant was independent of the partial hydrogen pressure and, consequently, the observed increase in the degree of cyclohexane isomerization with an increase in total pressure was caused by the increase in contact time, which was proportional to the total pressure with constant input rates. At 320 and 340°, the reaction rate constant decreased with an increase in the partial hydrogen pressure. The change in the relation of the rate constant of cyclohexane isomerization to partial hydrogen pressure with an increase in temperature from 320 to 430° could be caused by the reaction changing from the kinetic to the diffusion region. The purpose of the present investigation is the elucidation of this problem.

EXPERIMENTAL

A change from the kinetic to the diffusion region may be established from the change in the apparent activation energy with temperature. For this purpose we carried out a series of experiments at 320, 340, 380, 410 and 430° and various partial hydrogen pressures (Table 1).^{*} The logarithms of the rate constants ($\lg k_{pH_2}$) are plotted against the partial hydrogen pressures in Fig. 1. These experiments were carried out on the sample of industrial catalyst which was used in [1]. The rate constants in [1] and in the present work at 340 and 430° were found to be very close. Therefore, Fig. 1 also gives the logarithms of the rate constants at 340, 370, 400 and 430°, calculated from data in [1]. An examination of Fig. 1 shows that at all the temperatures investigated, the relation of the logarithm of the rate constant to the partial hydrogen pressure may be described approximately by the following equation:

$$\lg k_{pH_2} = \lg k_0 - cp_{H_2} \quad (1)$$

^{*}The apparatus and the investigation procedure were described previously [1].

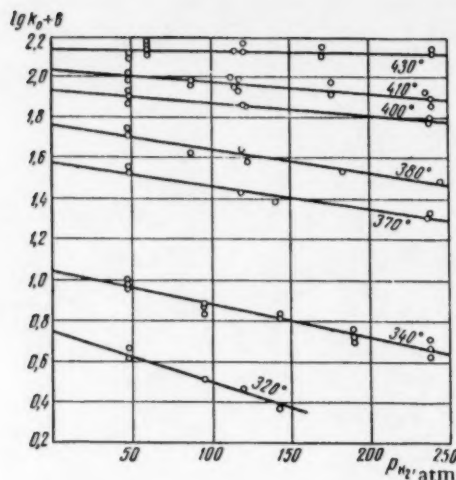


Fig. 1. Relation of logarithm of reaction rate constant to partial hydrogen pressure with k in $(\text{mole}/\text{cm})^{0.6} \cdot \text{sec}^{-1}$.

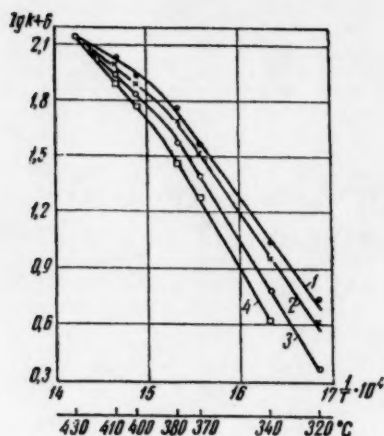


Fig. 2. Temperature dependence of logarithm of reaction rate constant: 1) k_0 ; 2) $k_{50 \text{ atm}}$; 3) $k_{150 \text{ atm}}$; 4) $k_{250 \text{ atm}}$.

where k_0 is the reaction rate constant extrapolated to $p_{\text{H}_2} = 0$ and c is an empirical constant depending on temperature.

On the basis of (1) and the order of the reaction with respect to cyclohexane found in [1] (see above), it is possible to write the following equation for the reaction rate w over the whole range of temperatures and pressures investigated:

$$w = k_0 p_{\text{C}_6\text{H}_{12}}^{0.4} e^{-d p_{\text{H}_2}} \quad (2)$$

where $d = 2.303 c$.

The value of $\log k_0$ at different temperatures was determined by extrapolation of the lines in Fig. 1 to $p_{\text{H}_2} = 0$ and the values of d from the slopes of these lines. The values of k_0 and d found are given in Table 2. The data in Table 2 show that the values of the constant d decrease with a rise in temperature and become close to zero at 430° .

The values of $\log k_0$ are plotted against $1/T$ in Fig. 2 (curve 1). An examination of Fig. 2 shows that over the temperature range 320 – 380° , the relation of $\log k_0$ to $1/T$ is expressed by a straight line. The apparent activation energy of the reaction calculated from the slope of this line equals 30 kcal/mole . The high absolute value of this activation energy indicates the absence of an appreciable effect of diffusion factors on the reaction rate.

An increase in temperature above 380° leads to a bend in the line with a sharp fall in slope, indicating that the reaction passes into the diffusion or transition region. The order of reaction n with respect to cyclohexane at 430° (0.4) supports the hypothesis on the inner diffusion region. An order with respect to the reagent of $n = 1$ corresponds to the inner diffusion region [2]. If the values of $\log k_{p_{\text{H}_2}}$ calculated from the line in Fig. 1 at pressures of 50 , 150 , and 250 atm are plotted on Fig. 2 (curves 2, 3, and 4), then it is found that over the temperature range 320 – 380° , they are also described by lines whose slopes increase as the pressure increases. In this case also there is a bend on the lines with a decrease in slope at a temperature above 380° . This may be regarded as confirmation of the fact that the reaction passes into the diffusion (or transition) region above 380° over the whole of the pressure range investigated. Consequently, retardation of cyclohexane isomerization with an increase in the partial hydrogen pressure is characteristic of the kinetic region; this retardation gradually disappears when the reaction passes into the diffusion region.

TABLE 1

Isomerization of Cyclohexane

Experiment No.	Partial pressure in atm		Rate in mole/hr		τ in sec*	Dilution $H_2:C_6H_{12}$	Catalyzate composition in weight % ***					$k_{PH_2} \cdot 10^6$ (mole/ cc) ^{0.6} sec ⁻¹
	C_6H_{12}	H_2	C_6H_{12}	H_2			C_6H_{12}	$C_3H_7CH_3$ <i>a</i>	C_4H_{10} <i>b</i>	$a+b$	$\frac{b}{a+b} \cdot 100$	
320°												
205	2,41	47,6	0,0670	1,33	199	19,8	70,8	27,6	1,6	29,2	5,5	4,06
212	2,45	47,6	0,0665	1,29	204	19,4	67,5	31,1	1,4	32,5	4,4	4,55
209	2,47	95,0	0,0686	2,64	200	38,5	76,8	21,7	1,5	23,2	6,4	3,22
210	2,50	119	0,0692	3,28	201	47,4	79,1	19,8	1,1	20,9	5,3	2,90
208	2,46	143	0,0696	4,06	195	58,3	83,8	15,3	0,9	16,2	5,5	2,29
340°												
201	2,38	47,6	0,134	2,68	95,4	20,0	66,3	31,8	1,9	33,7	5,6	9,68
206	2,45	47,6	0,134	2,60	98,2	19,4	66,8	31,1	2,1	33,2	6,3	9,39
186	2,34	95,2	0,136	5,50	93,0	40,5	73,8	25,1	1,1	26,2	4,2	7,47
197	2,44	95,1	0,138	5,37	95,0	38,9	76,0	22,5	1,5	24,0	6,3	6,93
191	2,30	143	0,129	8,00	95,7	62,0	76,8	21,8	1,4	23,2	6,0	6,30
193	2,41	143	0,129	7,63	100	59,2	76,8	21,8	1,4	23,2	6,0	6,26
189	2,50	190	0,138	10,5	97,3	76,0	80,0	18,6	1,4	20,0	7,0	5,62
199	2,46	190	0,134	10,4	98,3	77,6	80,8	17,5	1,7	19,2	8,8	5,25
194	2,31	237	0,128	13,2	96,7	103	83,0	15,9	1,1	17,0	6,5	4,52
204	2,28	257	0,141	4,7	86,7	104	83,1	15,5	1,4	16,9	8,3	5,07
380°												
211	2,41	47,6	0,911	18,0	13,3	19,7	72,9	26,2	0,9	27,1	3,3	53,1
218	2,39	47,6	0,869	17,3	13,9	19,9	72,9	26,3	0,8	27,1	3,0	51,2
214	2,49	87,5	0,898	31,6	14,0	35,2	77,9	21,2	0,9	22,1	4,1	41,8
213	2,47	123	0,901	44,7	13,8	49,6	79,7	19,1	1,2	20,3	5,9	38,3
217	4,82	120	0,888	22,2	27,3	25,0	70,3	27,3	2,4	29,7	8,1	43,4
216	4,99	185	0,917	34,0	27,4	37,1	76,4	21,4	2,2	23,6	9,3	34,7
215	5,08	245	0,926	44,6	27,6	48,2	79,2	18,8	2,0	20,8	9,6	30,5
410°**												
223	2,43	47,6	1,49	29,0	7,89	19,6	69,9	29,1	1,0	30,1	3,3	98,3
225	2,57	87,4	1,49	50,5	8,34	34,0	70,4	28,0	1,6	29,6	5,4	94,5
226	2,65	122	1,54	71,1	8,29	46,1	73,5	23,9	2,6	26,5	9,8	85,8
224	9,65	115	1,51	18,0	30,9	42,0	55,0	41,3	3,7	45,0	8,2	89,8
229	9,96	180	1,51	27,3	31,8	18,1	57,4	35,4	7,2	42,6	17,0	83,3
228	10,1	240	1,52	36,0	32,1	23,8	62,3	30,8	6,9	37,7	18,3	72,9
235	2,50	47,5	1,56	29,6	7,74	19,0	68,6	29,5	1,9	31,4	6,1	107
236	2,96	87,0	1,58	46,5	9,01	29,4	70,9	26,3	2,8	29,1	9,6	93,4
230	2,71	122	1,63	73,6	8,00	45,2	73,0	24,0	3,0	27,0	11,1	92,1
234	13,1	112	2,43	20,7	26,0	8,54	63,5	32,7	3,8	36,5	10,4	101
231	12,8	177	2,34	32,3	26,4	13,8	64,4	30,0	5,6	35,6	15,7	95,8
232	13,0	237	2,32	42,3	27,0	18,3	66,9	26,8	6,3	33,1	19,0	87,3
430°												
219	5,46	59,5	2,18	23,8	11,7	10,9	63,3	35,0	1,7	36,7	4,6	131
222	5,54	59,5	2,25	24,1	11,5	10,7	61,9	36,4	1,7	38,1	4,5	140
227	5,40	59,6	2,19	24,2	11,5	11,0	60,4	37,0	2,6	39,6	6,6	145
241	5,55	59,5	2,26	24,3	11,5	10,7	60,6	36,5	2,9	39,4	7,4	147
221	10,4	115	2,19	24,0	22,3	11,0	53,2	43,0	3,8	46,8	8,3	134
220	9,99	172	2,10	36,1	22,3	17,2	53,4	41,5	5,1	46,6	10,9	130
233	10,9	171	2,36	37,0	21,7	15,7	53,5	38,3	8,2	46,5	17,6	140

* τ is the arbitrary contact time.

** The activity of the catalyst in experiments 223-229 was somewhat lower than in experiments 230-236.

*** Due to incomplete condensation of the catalyzate, its yield varied from 92-93% with the ratio $H_2: C_6H_{12} = 10-12$ to 83-85% when this ratio equalled 70-100.

TABLE 2

Values of Constants of Equation (2)

Temperature in °C	$k_0 \cdot 10^6$ (mole/cc) ^{0.6} · sec ⁻¹	$d \cdot 10^3$	Temperature in °C	$k_0 \cdot 10^6$ (mole/cc) ^{0.6} · sec ⁻¹	$d \cdot 10^3$
320	5,60	5,80	400	85,1	1,38
340	11,1	3,89	410	107	1,33
370	38,6	2,86	430	139	0,23
380	57,8	2,74			

TABLE 3

Isomerization of Cyclohexane at 340° and a Total Pressure of 50 atm on a Catalyst of Various Grain Sizes*

Grain size in mm	Rate in mole/hr		τ in sec	Dilution $H_2:C_6H_{12}$	Catalyzate composition in weight%					$k_{PH_2} \cdot 10^6$ in (mole/cc) ^{0.6} · sec ⁻¹
	C_6H_{12}	H_2			C_6H_{12}	$C_5H_8CH_3$ <i>a</i>	C_4H_{10} <i>b</i>	<i>a</i> + <i>b</i>	$\frac{b}{a+b} \cdot 100$	
3-5	0,284	5,42	47,4	19,1	75,6	23,6	0,8	24,4	3,3	14,3
3-5	0,141	2,65	96,3	18,8	48,6	48,4	3,3	51,4	6,4	16,0
1-2	0,294	5,31	38,6	18,0	79,4	20,1	0,5	20,6	2,7	15,0
1-2	0,144	2,61	78,5	18,1	57,7	40,7	1,6	42,3	3,8	16,0

*In experiments with a grain size of 3-5 mm, we used 184.1 g of catalyst (packed volume 73.0 cc) and in experiments with a grain size of 1-2 mm, a 147.8 g (packed volume 62.0 cc). The catalyst sample used was first kept in a stream of hydrogen at 450°, which lead to some increase in its activity.

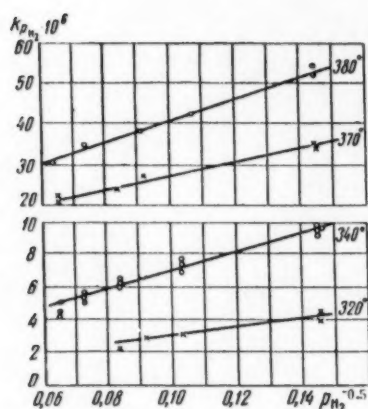


Fig. 3. Check of equation $k_{PH_2} = a + b \cdot p_{H_2}^{-0.5}$.

When the reaction occurs in the kinetic region, the isomerization rate should be independent of the catalyst grain size. Therefore, we also investigated the effect of catalyst grain size on cyclohexane isomerization rate at 340°. These experiments were carried out with catalyst grain sizes of 3-5 mm and 1-2 mm at pressures of 50 and 250 atm. The results of experiments at 50 atm are given in Table 3.

The data in Table 3 show that a decrease in the catalyst grain size did not affect the value of k_{PH_2} . An analogous result was obtained in experiments at 250 atm; with the given change in the catalyst grain size, the value of k_{PH_2} was found to be constant and equal to $6.0 \cdot 10^{-6}$ (g · mole/cc)^{0.6} sec⁻¹. Thus, the results of these experiments confirmed that the reaction occurs in the kinetic region at 340°.

In conclusion, we should note that the values of k_{PH_2} at 320-380° are also described by an empirical equation:

$$k_{PH_2} = a + b \cdot p_{H_2}^{-0.5} \quad (3)$$

The constants a and b in this equation, found from Fig. 3, are given in Table 4.

TABLE 4

Constants of Equation (3)

Temp. (°C)	$a \cdot 10^4$	$b \cdot 10^4$	Temp. (°C)	$a \cdot 10^4$	$b \cdot 10^4$
320	0,45	26,7	370	10,4	167
340	1,22	58,2	380	15,1	250

We used the data in Table 4 to calculate the values of k_{pH_2} at 1 atm ($k_1 = a + b$). Naturally, the values of k_1 obtained by this extrapolation differ from the values of k (at $p_{H_2} = 0$), found from equation (1). Nonetheless, a plot of $\log k_1$ against $1/T$ also gave a line whose slope corresponded to an apparent activation energy of 29 kcal/mole., i.e., extremely close to the value found previously (30 kcal/mole).

Laboratory assistant E. A. Udal'tsova and mechanic Yu. I. Ryzhov helped with the work.

SUMMARY

1. An investigation was made of the effect of temperature and catalyst grain size on the rate of cyclohexane isomerization to methylcyclopentane in the presence of an industrial WS_2 catalyst under a pressure of hydrogen in a flow system.

2. The reaction proceeded in the kinetic region over the temperature range 320-380°, but above 380° it passed into the diffusion (or transition) region. The apparent activation energy in the kinetic region was ~30 kcal/mole.

3. The retardation of cyclohexane isomerization with an increase in partial hydrogen pressure is not caused by diffusion factors and is characteristic of the kinetic region of the reaction.

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*Original Russian pagination. See C. B. translation.

MOLECULAR AND CRYSTAL STRUCTURE OF FERROCENEDISULFONYL CHLORIDE

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The investigation of di- and polysubstituted derivatives of ferrocene (C_5H_5)₂Fe by x-ray structural analysis is of considerable interest as it is not always possible to establish the position of substituents in ferrocene by available chemical methods or this requires a large amount of material. In addition, the relative position of substituents in not only one cyclopentadienyl ring, but also in different rings is interesting as according to available data, in different ferrocene derivatives this position is different: In dibenzoylferrocene and other diacylferrocenes, the substituents are in the 1,2' positions [1], while in di-p-chlorophenylferrocene, the p-chlorophenyl groups are probably in the 1,3' positions [2] (the positions of substituents in the ferrocene nucleus are denoted in accordance with Struchkov's method [3]).

In the present work we investigated ferrocenedisulfonyl chloride ($ClSO_2C_5H_4$)₂Fe, prepared in the laboratory of the Chemistry Faculty of the Moscow State University by Perevalova and Churanov [4]. Ferrocenedisulfonyl chloride forms fine, bright yellow platelets, which crystallize readily from dichloroethane and benzene and have t. decomp. 150°. In contrast to most aromatic sulfonyl chlorides, ferrocenedisulfonyl chloride is stable in air and may be dissolved in wet alcohol. As an example of the stability of the substance, we may quote the fact that one crystal of ferrocenedisulfonyl chloride was used to obtain diffraction patterns with molybdenum radiation for two months without appreciable change even though it was not covered with lacquer for protection against air. All this indicates the much lower polarity of the sulfur-chlorine bond in ferrocenedisulfonyl chloride in comparison with other aromatic sulfonyl chlorides.

On an optical goniometer it was possible to obtain only 001 and 00 $\bar{1}$ reflections (from the large faces of the platelet). The crystal was therefore set up for Laue diffraction patterns. The parameters of the crystal lattice were determined from an oscillating-crystal diffraction pattern: $a = 7.95 \pm 0.04$ Å; $b = 7.85 \pm 0.02$ Å; $c = 10.95 \pm 0.07$ Å; $\beta = 97^\circ \pm 1^\circ$; $V = 677.4$ Å³; $Z = 2$; $d_{x\text{-ray}} = 1.88$ g/cc (the monoclinic angle was found from a Laue diffraction pattern).

With a camera for photographing the reciprocal lattice and using unfiltered molybdenum radiation, we photographed 6 layer lines with rotation about the axis of the main zone ($h0l \div h\bar{5}l$), containing 700 reflections differing from zero, and the line $hk0$. From the systematic extinctions it was established that the space group was $P2_1/c$. Data on the space group and the number of molecules in the cell lead to the conclusion that the molecule occupies a particular position in the crystal with the iron atom at a center of inversion and, consequently, has a symmetry of $\bar{1}$ in the crystal while the iron atom has the coordinates (0, 0, 0). The molecule may only have this symmetry if the substituents (sulfonyl chloride groups) are in positions 1,1' (Fig. 1).

The intensities of the spots on the x-ray diffraction patterns were estimated visually. The angle factor was considered. In the construction of the projections of electron density and interatomic functions, the scale was chosen arbitrarily; the intensities were reduced to one scale by Wilson's method [5] for the calculation of space series.

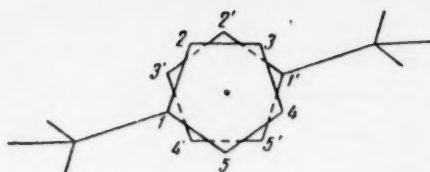


Fig. 1. Structural plan of the ferrocenedisulfonyl chloride molecule.

To determine the coordinates of the atoms, we began with the construction of the most convenient projection of the interatomic function on the xz plane. From this projection it was possible to obtain the coordinates of the sulfur and the chlorine atoms and two oxygen atoms, though a reliable assignment of the iron-oxygen maxima became possible only at a later stage of the investigation.

From the coordinates of the iron, sulfur, and chlorine atoms, we determined the signs (with the assumption that the atomic curves were similar) and constructed the projection of the electron density on the same plane. From this projection also we

could only find the coordinates of the sulfur, chlorine, and two oxygen atoms. As was found later, this is explained by the "inconvenient" position of the molecule in the cell from the point of view of constructing the projection (Fig. 2), as a result of which a number of atoms were superposed on each other in the projection (S and C_1 ; O_1 , C_5 and C_4 ; O_2 , C_2 and C_3). Geometric analysis was used for an approximate determination of the third coordinate (y) of the sulfur, chlorine, and oxygen atoms and subsequently to find the position of the carbon atoms. The following assumptions were made: the distances iron-carbon ring plane (1.66 Å), iron-carbon (2.04 Å), and carbon-carbon (1.40 Å) were assumed to be equal to the corresponding distances in ferrocene [6]. The bond lengths sulfur-carbon (1.81 Å), double sulfur-oxygen (1.49 Å), and sulfur-chlorine (2.03 Å) were assumed to be equal to the sums of the appropriate covalent radii [7]. It was also assumed that the sulfur atom is in the plane of the 5-membered ring, that this flat ring is symmetrical relative to the $S-C_1$ line, and that the angles in the sulfonyl chloride group are close to the tetrahedral value.

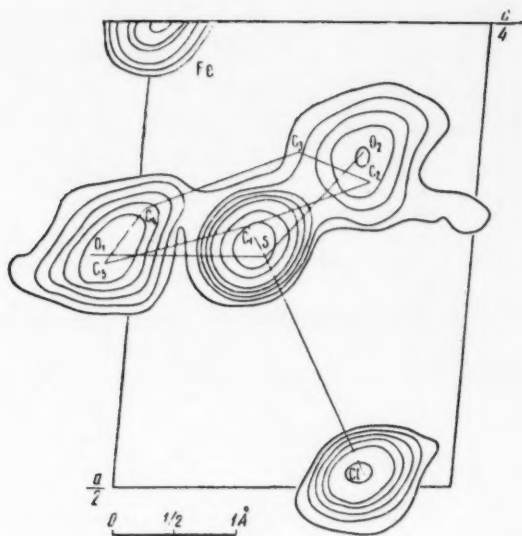


Fig. 2. Projection of electron density ρ on the xz plane. The electron-density scale is arbitrary. The isoelectronic curves are plotted for equal intervals of ρ , but at the maxima of the iron, sulfur, and chlorine atoms, the intervals between the curves are twice as great as in other places.

With the coordinates of the sulfur and chlorine atoms obtained in this way and also considering the iron atom, we determined the signs of the structural amplitudes of the type F_{hk0} , assuming the similarity of the atomic curves, and another projection of electron density on the xy plane was constructed. However, from this projection

TABLE 1

Coordinates of Atoms Obtained in Preliminary Stages of Analysis

Atom	From projections *			From space functions of interatomic vectors **		
	x/a	y/b	z/c	x/a	y/b	z/c
Fe	0	0	0	0	0	0
S	0,241	0,333	0,093	0,249	0,317	0,089
Cl	0,480	0,294	0,190	0,481	0,359	0,184
O ₁	0,243	0,469	0,479	0,268	0,379	0,467
O ₂	0,141	0,481	0,167	0,116	0,400	0,158
C ₁	0,203	0,135	0,079	(0,205)	(0,125)	(0,074)
C ₂	0,121	0,020	0,176	0,175	0	0,177
C ₃	0,112	0,829	0,125	(0,161)	(0,880)	(0,083)
C ₄	0,190	0,828	0,997	0,201	0,859	0,966
C ₅	0,247	0,017	0,968	0,256	0	0,983

*The y coordinates of the oxygen atoms and all the coordinates of the carbon atoms were found geometrically.

**The coordinates in brackets were obtained geometrically.

TABLE 2

Coordinates of Atoms found from Three-Dimensional Electron Density Series

Atom	x/a	y/b	z/c	Height of maximum in e/A ³ ***	Atom	x/a	y/b	z/c	Height of maximum in e/A ³ ***
Fe	0	0	0	42,4	C ₂ corr. *	0,130	0,991	0,140	—
S	0,243 ₂	0,306 ₉	0,096 ₂	18,7	C ₃	0,134	0,843	0,114	5,0
Cl	0,480 ₉	0,351 ₇	0,187 ₈	18,6	C ₄	0,195	0,838	0,005	6,7
O ₁	0,260	0,393	0,466	6,3	C ₅	0,253	0,996	0,478	5,8
O ₂	0,127	0,414	0,165	6,4	H ₂ **	0,09 ₉	0,02 ₃	0,24 ₁	—
C ₁	0,213	0,102	0,081	7,3	H ₃	0,07 ₉	0,74 ₉	0,15 ₇	—
C ₂	0,162	0,986	0,170	6,6	H ₄	0,19 ₈	0,72 ₁	0,44 ₅	—
					H ₅	0,30 ₈	0,03 ₆	0,39 ₅	—

*Coordinates corrected by allowing for the symmetry of the five-membered ring (see below).

**The coordinates of the hydrogen atoms were calculated as described below.

***The mean error in the determination of the heights of the maxima was ± 1.0 e/A³.

The distribution of the heights of the maxima indicates considerable thermal motion bearing the character of torsional vibrations of the molecules about the center of gravity.

it was possible to obtain only the coordinates of the sulfur and chlorine atoms, again due to considerable overlapping of the electron density maxima of a number of atoms on the projection. As a result of this initial state of the analysis, we established the approximate coordinates of all the atoms (Table 1), which lead to a plausible model of the molecule. To check the accuracy of the model chosen, we constructed a space function of the interatomic vectors, which completely confirmed the model adopted. The coordinates of the atoms found in this way are presented in Table 1.

To determine the coordinates of the atoms more accurately, we calculated a three-dimensional electron density series (Fig. 3), which clearly showed all the atoms apart from hydrogen. In the calculation of the structural amplitudes, the signs of which were used for the construction of F_{hkl} series, the atomic curves of all the atoms were considered to be similar. The single mean atomic curve for the given structure, which also allowed for the effective temperature factor, was established by Wilson's method [5] by comparison of F_{meas} and F'_{calc} .

where $F'_{calc} = 2 \sum_i Z_i \cos 2\pi(hx_i + ky_i + lz_i)$, i.e., the "trigonometrical" part of the structural amplitude.

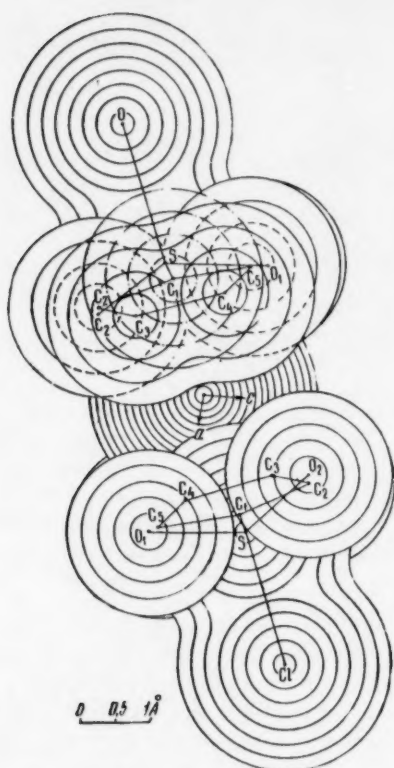


Fig. 3. Model of molecule from data of three-dimensional electron density series. Isoelectronic curves are given at intervals of $2.5 \text{ el}/\text{\AA}^3$ for the iron atom, $2 \text{ el}/\text{\AA}^3$ for sulfur and chlorine atoms, and $1 \text{ el}/\text{\AA}^3$ for oxygen and carbon atoms; the lowest line corresponds to a density of $2 \text{ el}/\text{\AA}^3$.

all five carbon atoms. On the other hand, there are no reasonable grounds for deviation of any of the carbon atoms from the plane, especially the second carbon atom, which has an equivalent analog in the ring (C_5). For these reasons, the coordinates of the second carbon atom were corrected in the following way. It was assumed that the carbon ring has an axis of symmetry, which is the line passing through the sulfur atom and the carbon atom connected to it ("first"). Since this line is actually inclined slightly to the plane found with the exception of the second carbon atom, the projection of this line on the plane was taken as the axis of symmetry. The operation of the axis obtained on the fifth carbon atom gave the corrected coordinates of the second carbon atom, which were adopted in subsequent analysis of the molecular and crystal structure.

The equation of the carbon ring plane obtained with allowance for the corrected second carbon atom has the form:

$$0,9024x - 0,1901y + 0,3869z - 1,605 = 0.$$

The deviations of individual atoms from this plane are as follows: $S \pm 0.01$; $C_1 - 0.02$; $C_{2\text{corr.}} + 0.01$; $C_3 - 0.01$; $C_4 + 0.03$; $C_5 - 0.01 \text{ \AA}$. The mean deviation is $\pm 0.02 \text{ \AA}$.

All the atoms were considered in the calculation according to the coordinates found from the three-dimensional interatomic function. It was found that the mean effective single atomic curve is expressed as $f = e^{-3.2 (\sin \theta / \lambda)^2}$.

The coordinates of the atoms obtained from the space function of electron density are given in Table 2.

The equation of the ring plane was found to check the planarity of the carbon ring by the method of least squares. In the calculation it was assumed that the sulfur atom also lies in this plane. The calculation was carried out in an absolute rectangular system of coordinates (Ox^*yz , where Ox^* is normal to Oyz). The equation of the carbon ring plane constructed in this way has the form: $0.9309x - 0.1843y + 0.3158z - 1.648 = 0$. The deviations of individual atoms from this plane are characterized by the following values: $S + 0.05$; $C_1 + 0.02$; $C_2 - 0.10$; $C_3 + 0.09$; $C_4 + 0.03$; $C_5 + 0.06 \text{ \AA}$. The mean error is $\pm 0.06 \text{ \AA}$. The large mean deviation and the scatter of the atoms relative to the mean plane and also the extreme deviation from the mean value in the lengths of the C_2-C_3 and C_2-Fe bonds lead us to the opinion that it was precisely the great error in the determination of the coordinates of the second carbon atom which caused the great mean deviation of the atoms from the plane. In actual fact, construction of the plane without allowance for C_2 gave the following equation:

$$0,9053x - 0,1900y + 0,3802z - 1,608 = 0$$

The deviation of the atoms from this plane are determined by the following values: $S + 0.02$; $C_1 - 0.02$; $C_3 - 0.01$; $C_4 + 0.02$; $C_5 - 0.02 \text{ \AA}$. The mean error is $\pm 0.02 \text{ \AA}$. The deviation of the second carbon atom from this plane is -0.22 \AA .

It should be emphasized that the exclusion of any other carbon atom in the calculation of the plane with the second one included does not give a lower scatter and mean error in comparison with the results obtained in the construction of the plane for

TABLE 3

Interatomic Distances and Valence Angles in the Ferrocenedisulfonyl Chloride Molecule

Interatomic distance in Å	Δ	Valence angle in deg.	Δ	Interatomic distance in Å	Δ	Valence angle in deg.	Δ
S—Cl 2,06	—	O ₁ SO ₂ 121	—	C ₄ —C ₅ 1,37	—0,01	SC ₁ C ₂ 127	0
S—O ₁ 1,59	+0,04	O ₁ SC ₁ 101	—1,5	C ₅ —C ₁ 1,46	+0,08	SC ₁ C ₅ 127	0
S—O ₂ 1,50	—0,05	O ₂ SC ₁ 104	+1,5	C—C 1,38	$\pm 0,06$	SCC 127	0
S—O 1,55	$\pm 0,05$	OSCl 102,5	$\pm 1,5$	C ₁ —Fe 1,98	—0,01	C ₁ C ₂ C ₃ 104	—3
S—C ₁ 1,64	—	ClSC ₁ 102	—	C ₂ —Fe 1,97	—0,02	C ₂ C ₃ C ₄ 115	+8
C ₁ —C ₂ 1,46	+0,08	O ₁ SC ₁ 102	—3	C ₃ —Fe 1,97	—0,02	C ₃ C ₄ C ₅ 106	—1
C ₂ —C ₃ 1,28	—0,10	O ₂ SC ₁ 108	+3	C ₄ —Fe 2,00	+0,01	C ₄ C ₅ C ₁ 104	—3
C ₃ —C ₄ 1,35	+0,03	OSC 105	± 3	C ₅ —Fe 2,05	+0,06	C ₅ C ₁ C ₂ 107	0
				C—Fe 1,99	$\pm 0,02$	CCC 107	± 3

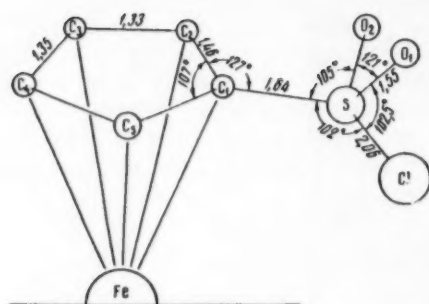


Fig. 4. Geometry of the ferrocenedisulfonyl chloride molecule from data from the present investigation.

The coordinates of the hydrogen atoms were calculated with the assumption that they lie on a line passing through the center of the five-membered ring and the corresponding carbon atom at a distance of 1.09 Å from the latter. The interatomic distances and valence angles obtained from the coordinates of the atoms given in Table 2 (the corrected values were used for C₂) are given in Table 3.

The accuracy of the results obtained was estimated from formulas proposed by Vainshtein [8], and was ± 0.005 Å for sulfur and chlorine atoms and ± 0.02 Å for oxygen and carbon atoms. These figures agree well with the mean deviation of sulfur and carbon atoms from the plane (± 0.02 Å) and with the error in the measurement of the iron-carbon distance (± 0.02 Å).

Analysis of the data obtained on the structure of the ferrocenedisulfonyl chloride molecule leads to the following conclusions. All the carbon atoms of the five-membered ring lie practically in one plane. The sulfur atom is in the same plane.

With the existing error in the determination of the coordinates of the carbon atoms of ± 0.02 Å, which gives a maximum error for the bond length of about ± 0.05 Å, it is impossible to assign any particular value to the different lengths of the individual bonds. However, if we make the natural assumption that the five-membered ring of the molecule examined has a plane of symmetry, then we arrive at the scheme shown in Fig. 4; this shows that the C₁—C₂ and C₁—C₅ bonds (1.46 Å), which are adjacent to the atom bearing the substituent, are substantially longer than the other bonds of the ring (1.38 and 1.35 Å) and the mean carbon-carbon bond length found for ferrocene [6] (1.403 ± 0.040 Å). Moreover, in ferrocenedisulfonyl chloride, the iron-carbon (1.99 ± 0.02 Å) and carbon ring plane-iron distances (1.61 Å) are also short in comparison with the corresponding distances found for ferrocene (2.045 ± 0.024 Å and 1.66 Å). The mean angle in the five-membered ring ($107 \pm 3^\circ$) agrees satisfactorily with the angle in a right pentagon (108°). A comparison of the valence angles of the sulfur atom (see Table 3) with the tetrahedral angle ($109^\circ 28'$) indicates that the sulfur atom has the configuration of a distorted tetrahedron.

The sulfur-carbon distance, which equals 1.64 Å, is appreciably short relative to the sum of the covalent radii of sulfur and carbon (1.81 Å) and also in comparison with data for, for example, β -isoprene sulfone [9] (1.75 ± 0.02 Å). The sum of the covalent radii for a sulfur-carbon double bond is 1.59 Å. For a series of sulfur-carbon compounds it is found to equal from 1.54 to 1.56 Å [9]. The lengths of the sulfur-oxygen bonds (1.55 ± 0.05 Å) are high in comparison with the sum of the covalent radii for a sulfur-oxygen double bond (1.49 Å) and relative to data for β -isoprene sulfone (1.44 Å). The sulfur-chlorine distance (2.06 Å) is somewhat greater than the length of a sulfur-chlorine covalent bond (2.03 Å) and considerably less than the sum of the ionic radii ($S^{+6} + Cl^{-1} = 2.15$ Å). The shortening of the sulfur-carbon bond and the lengthening of the sulfur-oxygen double bonds

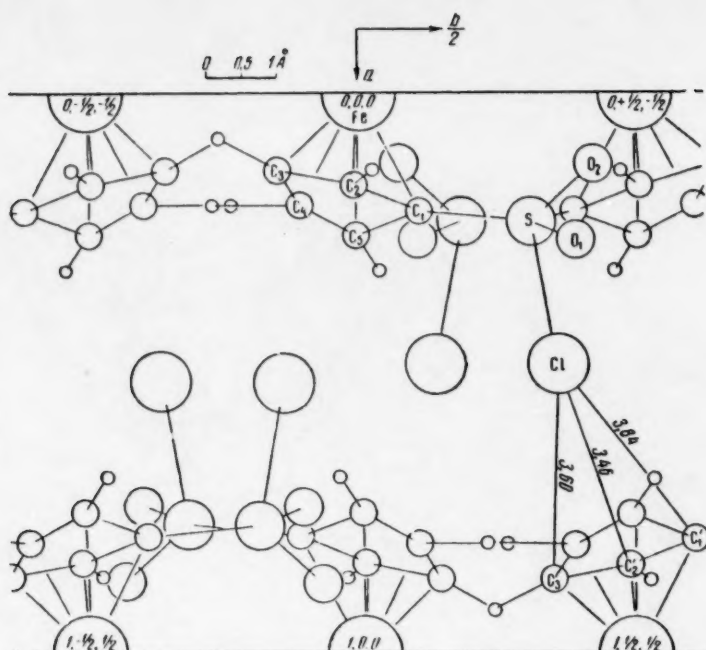


Fig. 5. Plan of the packing of the ferrocenedisulfonyl chloride molecules in the crystal and the shortest intermolecular distances, *xy* projection.

indicates an intimate electronic interaction of the sulfonyl chloride group with the ferrocene nucleus. The consequence of this interaction is apparently the shortening of the carbon-carbon and carbon-iron bonds in the ferrocene nucleus in comparison with ferrocene itself and the low lability of the chlorine atom in the sulfonyl chloride group. The similarity of the sulfur-chlorine bond length to that of a covalent bond indicates the very low polarity of this bond, which is confirmed by its considerable chemical stability.

The shortest intermolecular distances in the ferrocenedisulfonyl chloride crystal are shown in Figs. 5 and 6. The packing of the molecules is shown in Fig. 7.

The C_2-Cl (3.46 Å) and C_3-Cl (3.60 Å) distances agree satisfactorily with the tabular value of 3.5 Å [10]. The H_2-O_1 (2.60 Å) and H_2-O_2 (2.57 Å) distances also agree quite well with the the tabular value of 2.55 Å. The same applies to the C_2-O_2 distance (3.16 Å as compared with the tabular value of 3.10 Å). The other intermolecular distances appreciably exceed the sums of the radii and therefore are of no great interest. The coordination number of the molecule is 12. The packing factor $k = 0.64$ (for the calculation we used tabular values of the intermolecular radii and the mean values of the bond lengths and valence angles that we found).

The sulfonyl chloride group lies practically symmetrically to the plane of symmetry of the ferrocene nucleus. This is indicated particularly by the fact that the distances of the oxygen atoms from the carbon ring plane (0.58 and 0.67 Å for O_1 and O_2 , respectively) are identical within the limits of error of the bond lengths. This position of the sulfonyl chloride group is the most natural one as rotation of this group about the sulfur-carbon bond involves an anomalous decrease in the distance between the carbon-oxygen and carbon-chlorine atoms which are not bound by valences.

In conclusion the authors would like to thank A. I. Kitaigorodskii for attention to and interest in the work and E. G. Perevalova and S. S. Churanov for providing the ferrocenedisulfonyl chloride.

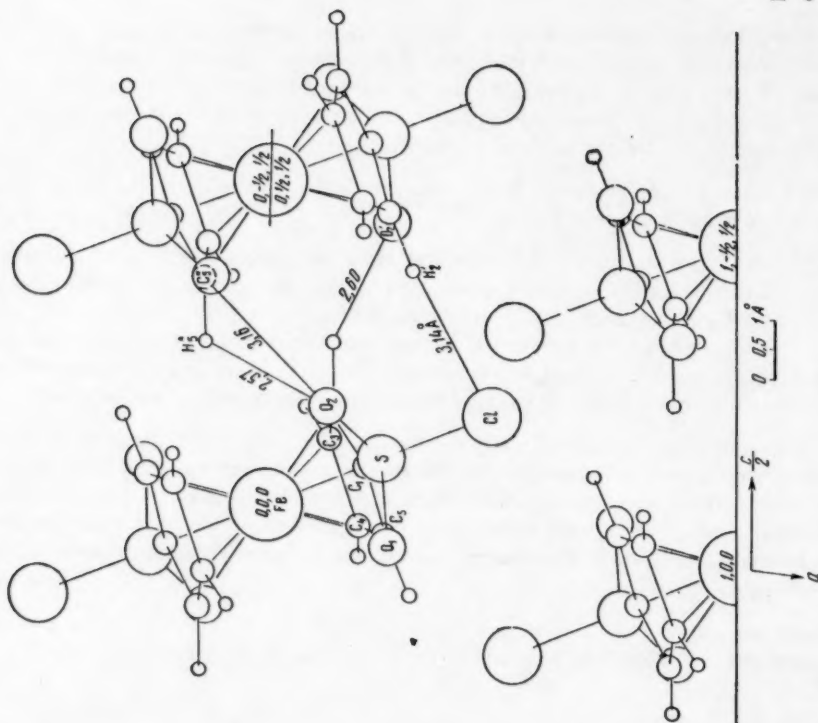


Fig. 6. Plan of packing of ferrocenedisulfonyl chloride molecules and shortest intermolecular distances, xz projection.

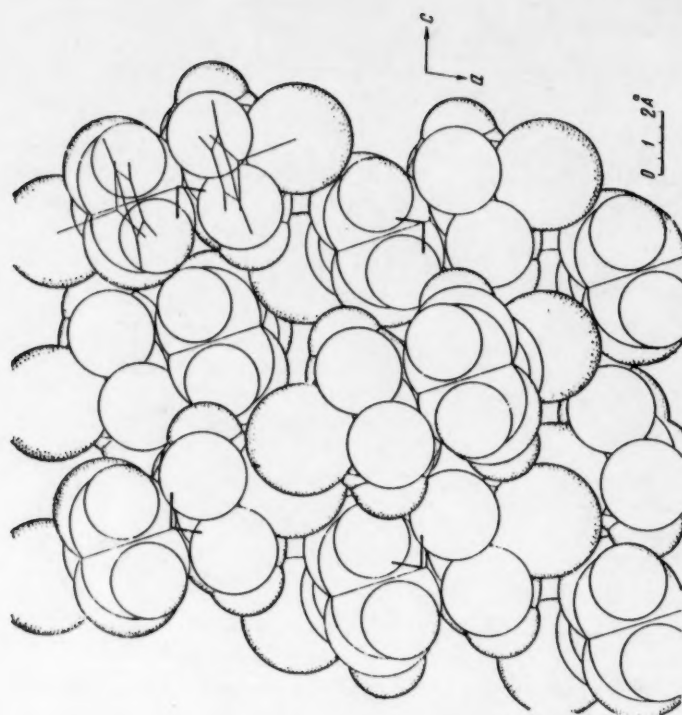


Fig. 7. Packing of ferrocenedisulfonyl chloride molecules. The atoms are drawn with the intermolecular radii. View perpendicular to the xz plane.

SUMMARY

1. The structure of ferrocendisulfonyl chloride was investigated. The interatomic distances and valence angles were found. The shortest intermolecular distances were calculated.

2. On the basis of the data obtained, it was shown that there is an intimate electronic interaction between the ferrocene nucleus and the sulfonyl chloride group, which leads to a redistribution of bond lengths and a decrease in the chemical activity of the chlorine in the sulfonyl chloride group in comparison with normal aromatic sulfonyl chlorides.

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CRYSTAL STRUCTURE OF A SOLID SOLUTION
CONTAINING 91.3% p-DIIODOBENZENE
AND 8.7% p-DIBROMOBENZENE

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From an x-ray diffraction investigation of solid solutions of the system p-diiodobenzene-p-dibromobenzene, it was established that the introduction of relatively small amounts of p-dibromobenzene ($5 \pm 1\%$ and above)* produces extensive rearrangement of the p-diiodobenzene structure with a change in the space group of the crystal symmetry. It was found that the system p-diiodobenzene-p-dibromobenzene is not a system with only a eutectic point, as was reported in the literature [1], but also has a peritectic point. Without considering now the detailed characteristics of the diagram of this system, which will be reported later, we describe the structure of a new crystalline phase which we detected in this system. The determination of this structure was necessary to elucidate the nature of the packing of molecules and the mechanism of phase conversions in the system studied.

The crystals were obtained from a melt with the composition 80.0% p-diiodobenzene and 20.0% p-dibromobenzene (the accuracy with which the composition of the melt was determined was $\pm 0.5\%$). The composition of the crystals obtained was 91.3% p-diiodobenzene and 8.7% p-dibromobenzene (the accuracy of the determination of the composition was $\pm 1\%$). The crystallization temperature $T_{cr} = 117.9^\circ$. The crystals were platelets, elongated along the *c* axis. The parameters of the rhombic elementary cell were determined from distant spots on oscillating-crystal x-ray patterns, obtained with unfiltered Cu radiation in an RKU-86 camera (diameter 86 mm, asymmetric insertion of film, rotation axes *b* and *c*, standard-NaCl powder, which was sprinkled onto the monocrystals which had first been immersed in shellac): $a = 17.04 \pm 0.01$ Å; $b = 7.428 \pm 0.002$ Å; $c = 5.900 \pm 0.002$ Å; $V = 746.76$ Å³. The space group, which was unequivocally determined by the systematic extinctions, was $V_h^{10} = Pccn$ with four molecules in the cell. The molecule occupies a particular position: its center of gravity coincides with the center of symmetry. Crystals of p-diiodobenzene belong to the space group $V_h^{15} = Pbca$ with four molecules per cell, which also occupy the centers of symmetry [2].

An x-ray investigation of the crystals was carried out by photographing the reciprocal lattice with unfiltered Mo radiation. We obtained developments of the zero layer lines with rotation about the *b* and *c* axes and visually estimated the intensities of 48 reflections of the *h0l* type and 64 reflections of the *hk0* type. In converting the intensities to structural factors, we considered only two intensity factors: Lorenz and polarization. The solution of the structure began with a construction of projections of the interatomic function on the *ab* and *ac* faces which gave the following coordinates for the iodine atom: $x = 0.169$; $y = 0.041$; $z = 0.294$. Starting from these values for the coordinates of the iodine atom, we determined the signs of the structural amplitudes and calculated the electron density projections on *ab* and *ac*. The coordinates of the iodine atom obtained in the two projections agreed well with those found from the maxima of the interatomic function: $x = 0.1691$; $y = 0.0388$; $z = 0.3062$. The carbon atoms did not appear very clearly, but the orientation of the molecule was established quite reliably. Recalculation of the structural amplitudes with allowance for the carbon atoms did not change any of the signs. This means that the possibilities of electron density projections was already exhausted.

*Which corresponds to a p-dibromobenzene content of $11 \pm 0.5\%$ and above in the melt.

TABLE 1

Coordinates of Symmetrically Independent Atoms

Atom	Coordinates in Å			Relative coordinates		
	x	y	z	x	y	z
I	2,880	0,288	1,806	0,1691	0,0388	0,3062
C ₁	1,18	0,12	0,74	0,069	0,116	0,126
C ₂	1,22	-0,39	-0,56	0,072	-0,053	-0,095
C ₃	0,04	-0,51	-1,30	0,002	-0,069	-0,221
H ₂	2,16	-0,70	-0,99	0,127	-0,094	-0,168
H ₃	0,07	-0,91	-2,31	0,004	-0,123	-0,391

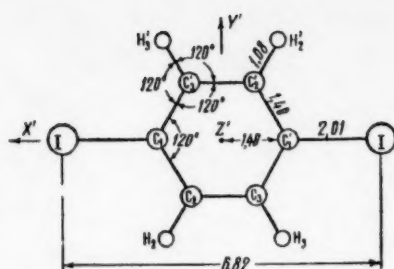


Fig. 1. Model of p-diiodobenzene molecule used for geometric analysis.

(0z) and 0y' axes, respectively, the iodine atom was superposed on its position found experimentally. We obtained the values $\varphi = 5^\circ 42'$ and $\omega = -32^\circ 2'$. The geometrical analysis was completed by determination of the optimal angle of rotation φ about the I-I line (0x' axis) so that the position of the iodine atom was established extremely accurately. The optimal position was considered to be that in which the value of the reliability factor R was minimal. For this purpose we calculated only the following structural amplitudes: 040; 080; 110; 130; 150; and 190, since they are extremely sensitive to a change in the values of γ with a change in the angle φ , while the coordinates x_C and z_C are determined much better from projections. The following values of the reliability factors were obtained for five values of φ :

φ	60°	63°	65°	67°	70°
R	5,18%	4,85%	4,69%	4,77%	5,52%

Obviously, the value $\varphi = 65^\circ$ should be considered optimal.

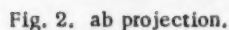
The coordinates of the carbon and hydrogen atoms found in this way are given in Table 1 and they agree well with the positions of the maxima on the electron density projections.

A comparison of these results with data for pure p-diiodobenzene [2] shows that the coordinates of the atoms in the two crystals are very similar but the packing of the molecules in the crystal is changed.

From the atomic curves of Viervoll and Ogrim [4] and the data in Table 1 we calculated the structural amplitudes F_{hk0} and F_{h0l} (hydrogen atoms were not considered). By comparing the calculated and measured values of the structural amplitudes by the method of least squares, we found the effective temperature factors $B_{hk0} = 3.53$ and $B_{h0l} = 4.17 \text{ Å}^2$. The difference in these values indicates considerable anisotropy of the thermal vibrations. From these temperature factors we recalculated the structural amplitudes and obtained the reliability factors of both zones: $R_{hk0} = 18.2\%$ and $R_{h0l} = 18.1\%$. If the carbon atoms are ignored, then the reliability factor increases: $R_{hk0} = 21.6\%$ and $R_{h0l} = 23.6\%$. Consequently, the coordinates of the carbon atoms were determined accurately on the whole and the geometrical analysis actually improved the results of the electron density projection. We

A geometric analysis was carried out for further refinement of the orientation of the molecule. We assumed that the benzene ring is a right planar hexagon with a side of 1.40 Å and the iodine atoms lie on a continuation of its diameter. The position of the hydrogen atoms was adopted in accordance with the conditions: C-H = 1.08 Å; angle H-C-C = 120° . According to experiment, the intramolecular I-I distance equals 6.82 Å. With the diameter of the benzene ring equal to 2.80 Å, this leads to a I-C bond length of 2.01 Å (the length of the I-C bond in pure p-diiodobenzene equals 2.02 Å [2] and the Br-C bond in pure p-dibromobenzene is 1.84 Å [3]).

As is shown in Fig. 1, we choose the axes of the coordinates 0x'y'z' of the molecule and superposed them initially on the 0xyz axis of the crystal. By rotations of ψ and ω about the 0z'



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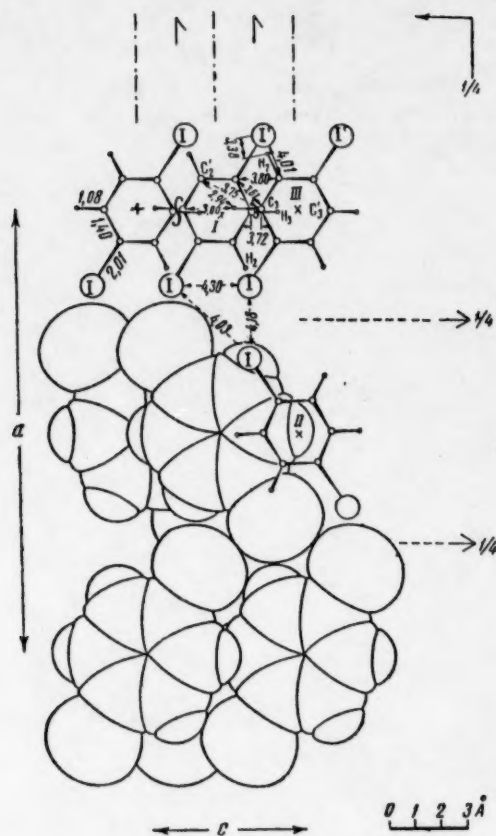


Fig. 3. *ac* projection.

TABLE 2

Shortest Intermolecular Distances

Atoms	Distance in Å	Sum of radii in Å	Difference in Å	Atoms	Distance in Å	Sum of radii in Å	Difference in Å
I (I) . . . I (II)	4,03	4,24	0,21	C ₂ (I) . . . C ₃ (III)	3,75	3,70	0,05
I (I) . . . I (III)	4,30	4,24	0,06	C ₁ (I) . . . C ₂ (III)	3,80	3,70	0,10
I (II) . . . I (III)	4,18	4,24	0,06	I (I) . . . C ₂ (III)	4,01	3,97	0,04
C ₁ (I) . . . C ₃ (III)	3,61	3,70	0,09	I (I) . . . H ₃ (III)	3,38	3,32	0,06
C ₃ (I) . . . C ₃ (III)	3,72	3,70	0,02	C ₃ (I) . . . H ₃ (III)	3,00	3,05	0,05
				C ₂ (I) . . . H ₃ (III)	2,94	3,05	0,11

SUMMARY

1. An accurate determination was made of the cell parameters of the solid solution containing 91,3% of *p*-diiodobenzene and 8,7% of *p*-dibromobenzene.
2. The coordinates the atoms were determined from electron density projections and geometrical analysis and these gave an I-C bond length of 2,01 Å.

3. The packing of the molecules in the crystal was analyzed and the shortest intermolecular distances and packing factor were determined.

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STUDY OF THE CORROSION AND
ELECTROCHEMICAL BEHAVIOR OF
STAINLESS STEELS DURING CATHODIC POLARIZATION
IN NITRIC ACID SOLUTIONS

COMMUNICATION 1. THE CHARACTERISTICS OF
DISSOLUTION OF STEELS

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From recently published work [1-7] it follows that an accurate scientific basis for the use of metals and alloys whose high corrosion resistance is caused by passivity requires a knowledge of the limits of stability of the passive state and also their corrosion and electrochemical behavior in the absence of passivating films. We undertook an investigation of the corrosion and electrochemical behavior of stainless steels under cathodic polarization in nitric acid solutions for a subsequent examination of the processes on stainless steels in the regions where the passive state is stable, during its destruction, and in the reactive state. We previously demonstrated the possibility of the destruction of the passive state of stainless steels and the subsequent production of cathodic electrochemical protection under the conditions studied [4].

EXPERIMENTAL

The passive state of stainless steels was destroyed and the steels were maintained in an active state in nitric acid solutions by means of cathodic polarization by an external current source. To study the limits of stability of the passive state of steels and their behavior in the active state, we determined the relations of the corrosion rates to the potential and the cathode polarization curves. These relations were obtained by polarization of samples with a direct current, which had a definite strength for each sample. From the measured losses in weight of the steel samples and also the mean potentials during the experiment time at each given polarization current density, we constructed the relations of the corrosion rates, calculated from the losses in weight, to the polarization current density and the potential. These relations were the anode and cathode polarization curves. All potentials were corrected to the hydrogen scale with allowance for the diffusion potentials. The subjects for investigation were ordinary construction stainless steel in the form of cylindrical samples. The chemical composition and structure of the steels corresponded to GOST 5632-50.

The samples were held with a screw thread in a special insulated holder which made it possible to supply current to them. The current source was a VSA-5 single-phase, two-stage selenium rectifier with continuous control of the rectified voltage. The investigations were carried out with solutions prepared with chemically pure nitric acid and distilled water in a thermostat.

A study of the effect of various factors on the corrosion and electro-chemical behavior of stainless steels under cathodic polarization in nitric acid solutions showed that there were characteristic relations of the corrosion

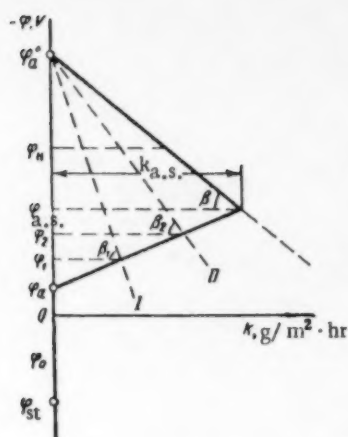


Fig. 1. Typical potential dependence of the corrosion rate of stainless steels under cathodic polarization in nitric acid solutions.

steel remains in the passive state at a potential of φ_0 . According to Bonhoeffer [8, 9], it may be considered that a displacement of the potential from φ_{st} to φ_0 leads to a decrease in the thickness of the passivating film, whose impermeability remains unimpaired. When the potential φ_a is reached, reduction of the passivating oxide film becomes possible, i.e., the disruption of its impermeability becomes possible and this leads to a change in the state of the surface. The change in the state of the steel surface at the potential φ_1 leads to a decrease in the anode polarizability $\tan \beta_1$ and corrosion of the steel at an appreciable rate. At the more negative potential φ_2 , the further activation of the steel surface leads to an even greater decrease in the anode polarizability $\tan \beta_2$ and a further increase in the corrosion rate. Finally, at the potential $\varphi_{a.s.}$, the whole of the steel surface becomes active, the anode polarization becomes minimal ($\tan \beta$), and the corrosion rate becomes maximal ($k_{a.s.}$). A displacement of the potential to values more negative than $\varphi_{a.s.}$ does not lead to a further change in the state of the steel surface as the protective oxide layer had been completely removed from its surface at the potential of the active state ($\varphi_{a.s.}$). Displacement of the potential to values more negative than $\varphi_{a.s.}$ leads to suppression of the dissolution of the steel, i.e., to cathodic electrochemical protection.

On the observed potential dependence of the corrosion rate, the slope of the section of the anode curve ($\tan \beta$) characterizes the anode polarizability of the steel in the active state and is a measure of the ease of ionization of the steel from the active state. The activation potential is the lower limit of stability of the passive state, while the potential of the active state, which is sometimes called the passivation potential [3], characterizes the beginning of passivating adsorption on the steel. We provisionally characterized the state of the surface of partly activated steel — in the region of potentials from φ_a to $\varphi_{a.s.}$ — by the fraction of active surface (α) and in the first approximation, evaluated it as the ratio of the corrosion rate at the given potential to the corrosion rate at the potential of the active state ($k_{a.s.}$).

For an actual case of the corrosion of steel under cathodic polarization, the simplified method we adopted for estimating the fraction of active surface obviously can only give high values of α .

By plotting polarization curves it was established that the anode and cathode curves are readily reproducible at potentials more negative than φ_H (Fig. 1), below which the reproducibility of the polarization curves is disrupted. The potential φ_H lies at a somewhat more negative value than the potential of the active state. The displacement of the potential φ_H toward negative values from $\varphi_{a.s.}$ is determined by the composition of the steel, acid concentration, and temperature. At more positive values than φ_H , the potentials of the steels either remain constant or the maximum increases by 40 mv after 30 min. Thereupon, the surfaces of the electrodes are gradually covered with a brown deposit, which is readily removed mechanically. This deposit, which is difficultly soluble in nitric

rate to potential and acid concentration. Chemical analysis of the corrosion products showed that the components of the steels dissolved in the ratio in which they occurred in the alloy. The corrosion of steels under cathodic polarization in HNO_3 solutions was of a uniform nature. With a constant potential, the steels were destroyed at a rate which was constant with time.

Effect of steel potential. The essential form of the relation between the corrosion rate of steels and the potential is shown in Fig. 1. This figure shows that for stainless steels under cathodic polarization in nitric acid, their passive state is destroyed at a definite potential — the activation potential (φ_a). When the potential is made more negative than this value, the corrosion rate increases (negative protection effect), reaches a maximum value at another definite potential — the potential of the active state ($\varphi_{a.s.}$), and then falls (positive protection effect). The increase in the steel corrosion rate when the potential is displaced toward negative values is due to a change in the state of the steel surface with a change in its potential.

At the stationary potential (φ_{st}), the steel is in the passive state, which may be explained by the presence of strong retardation of the anode process, and the anode polarizability equals infinity. We should note that the corrosion rate of stainless steels in the passive state is so low (10^{-6} – 10^{-5} A/cm²) that we consider it to be equal to zero. The

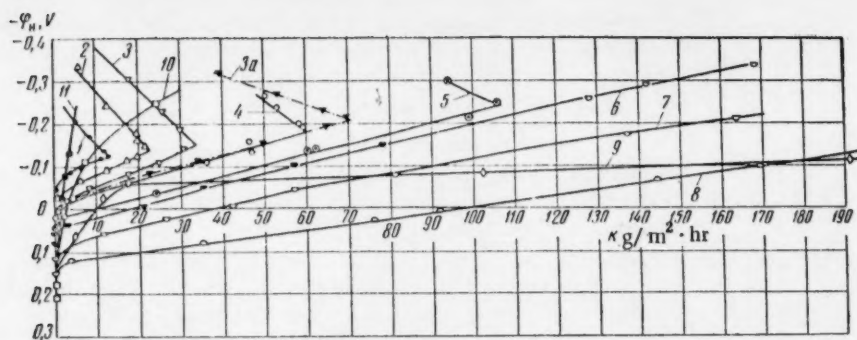


Fig. 2. Potential dependence of corrosion rate of 1Kh18N11B steel at 20° in nitric acid solutions: 1) 1%; 2) 2%; 3) 3%; 3a) 3% with stirring at 2500 rev/min; 4) 5%; 5) 8%; 6) 12%; 7) 20%; 8) 29%; 9) 35%; 10) 40%; 11) 50%.

acid, is evidently a mixture of carbides and elements present in the steel. In the region more negative than φ_H , the potentials of the steels decrease with time. Thereupon, gas bubbles grow on the surface of the steel electrodes and there is sometimes vigorous gas evolution from the whole surface. This region of potentials is characterized by poor reproducibility of the experimental points in parallel experiments. The experimental points on the anode and cathode polarization curves in the region of potentials more negative than φ_H are the mean values of the minima from three parallel experiments. Subsequently, we will mainly consider processes on stainless steels in nitric acid solutions in the region of potentials more positive than φ_H .

Effect of acid concentration. A change in the nitric acid concentration has a great effect on the limits of stability of the passive state, determined by the activation potentials, and on the corrosion behavior of activated steels. An examination of the potential dependence of the corrosion rate (Fig. 2) shows that stainless steel may be converted to the active state in nitric acid solutions of various concentrations up to 50%.

We were unable to activate steel by cathodic polarization in concentrated nitric acid solutions at 20°. In this case the anode polarization curves merged with the ordinate axis, indicating the existence of a definite nitric acid concentration above which steel may not be activated by a cathode current for a long time. Electrochemical cathodic protection, i.e., a decrease in the corrosion rate with a displacement of the potential toward negative values, is observed for dilute (no higher than 8%) nitric acid solutions. It is possible that stainless steel may be protected cathodically in more concentrated nitric acid solutions. The activation potentials of stainless steels increase with an increase in the concentration of hydrogen ions in the nitric acid solution. The pH dependencies of the activation potentials are different for dilute, completely dissociated (< 18–20%) and more concentrated solutions of nitric acid (> 20%) containing homeopolar molecules.* For solution concentration below 20%, the pH dependence of the activation potential of 1Kh18N11B steel at 20° is given by: $\varphi_A = +0.026 - 0.0095 \text{ pH}$. For 20% and more concentrated solutions of HNO_3 : $\varphi_A = -0.46 - 1.07 \text{ pH}$.

The activation potentials of stainless steels are displaced toward positive values with an increase in solution temperature.

With an increase in nitric acid concentration, the corrosion rate of stainless steels, cathodically polarized to a definite potential, changes, passing through a maximum (Fig. 3). The position and size of the corrosion-rate maximum depend on the potential, temperature, and steel composition.

The relations of the fraction of active surface and anode polarizability of 1Kh18N11B steel in the active state to acid concentration, which are given in Figs. 4 and 5, show why the change in corrosion rate has this character. At a constant potential, an increase in acid concentration produces acceleration of steel solution on the active surface ($\tan \beta$ decreases) with simultaneous contraction of the active sections (the fraction of active surface decreases). The opposing action of these two factors leads to the situation that with an increase in acid concentration, the corrosion rate of steel activated to a definite potential first increases, reaches a maximum at some

*Data on the degree of dissociation of nitric acid solutions are given in [10, 11].

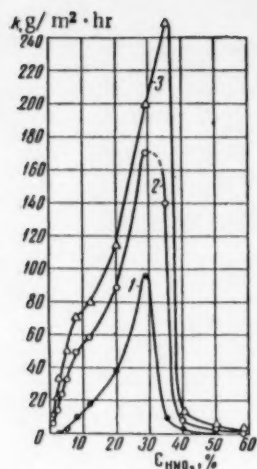


Fig. 3. Relation of corrosion rate of 1Kh18N11B stainless steel, polarized to a definite potential, to nitric acid concentration at 20°. 1) $\varphi = \pm 0.0$ V; 2) $\varphi = -0.18$ V; 3) $\varphi = -0.15$ V.

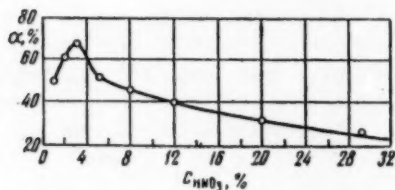


Fig. 4. Relation of the fraction of active surface of 1Kh18N11B steel at a potential of -0.1 v and 20° to nitric acid concentration.

Effect of temperature and stirring of acid. By a study of the effect of temperature on the corrosion and electrochemical behavior of stainless steels under cathodic polarization in nitric acid solutions, it was established that an increase in temperature changes the potentials of activation and the active state, the anode polarizability in the active state, and the fraction of active surface. These changes proceed in the same directions as with an increase in acid concentration. The temperature dependencies of the corrosion rate (an example for 3% nitric acid is given in Fig. 7) makes it possible to determine whether the solution of activated stainless steel is controlled by

definite acid concentration, and then falls to low values. The change in position and size of the corrosion-rate maxima in relation to potential, steel composition, and temperature may be regarded as the result of a difference in the rate of change of the fraction of active surface and the anode polarizability of the steel in the active state with an increase in the acid concentration.

With an increase in acid concentration, the potentials of the active state decrease, indicating broadening of the potential region in which steels are partially passivated. The analytical relation of the potential of the active state to nitric acid concentration for 1Kh18N11B steel at 20° may be expressed by the equation: $\varphi_{a.s.} = -0.11 - 0.015c$, where c is the acid concentration in percent. This equation was derived from experimental results (Fig. 2) for dilute (< 10%) acid solutions. Assuming that this equation also applies to more concentrated solutions, we determined $\varphi_{a.s.}$ and then used Fig. 2 to determine the maximum corrosion rates of steel in the active state ($k_{a.s.}$), required for calculating the fractions of active surface in more concentrated solutions. The calculation involving this assumption evidently gave high values for the fraction of active surface as we could not reach the beginning of cathodic protection of steel experimentally in 12-40% nitric acid solutions even at potentials which were more negative than the potential of the active state obtained hypothetically from the given formula.

A characteristic of the corrosion behavior of stainless steels in nitric acid solutions is the fact that in the completely active state, i.e., in the potential region in which there is cathodic protection, the rate of corrosion, like that of iron, is many times greater than in sulfuric acid solutions with the same content of hydrogen ions. This is demonstrated for chromium steels by Fig. 6 and for chromium-nickel steels, by a comparison of our results (Fig. 2) with those presented in [3]. We should also note that the potential dependence of the corrosion rate of stainless steels in nitric acid solutions is close to linear. In sulfuric acid solutions, analogous relations have a semilogarithmic character [3].

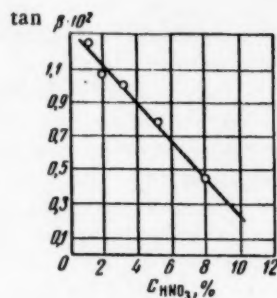


Fig. 5. Relation of anode polarizability of 1Kh18N11B steel in the active state at 20° to nitric acid concentration.

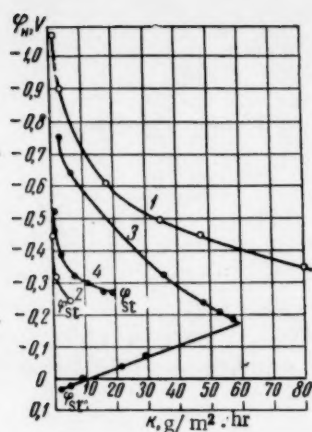


Fig. 6. Potential dependence of the corrosion rate of iron and 1Kh13 steel in 3% nitric and sulfuric acid solutions: HNO₃: 1) Fe; 3) 1Kh13; H₂SO₄: 2) Fe; 4) 1Kh13.

coefficients of the corrosion rates of stainless steel in 3% nitric acid with different potentials.

TABLE 1

Temperature Coefficients of the Corrosion Rate of 1Kh18N11B Steel in 3% Nitric Acid at Different Potentials

φ	-0,05	-0,1	-0,15	-0,20	-0,25
k_{20°	1,89	1,41	1,29	1,31	1,39
k_{10°					

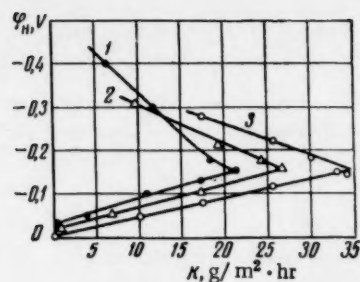


Fig. 7. Potential dependence of the corrosion rate of 1Kh18N11B steel in 3% nitric acid at different temperatures: 1) 3°; 2) 10°; 3) 20°.

the rate of electrode reactions or the rate of diffusion of reagents or corrosion products. It is normally considered that for chemical reactions, the reaction rate increases by a factor of 2-4 with a temperature increase of 10° [12], while the corresponding increase for diffusion processes is 10-30% [13]. Table 1 gives the temperature

TABLE 2

Temperature Coefficients of the Corrosion Rate of 1Kh8N11B Steel at $\varphi = 0.1$ v in Nitric Acid Solutions

C_{HNO_3} in %	5	12	20	29	40
$\frac{\kappa_{35^\circ}}{\kappa_{25^\circ}}$	1,5	1,75	1,98	0,67	0,42

The temperature coefficient of the corrosion rate of steel in 3% acid at the potential of the active state equalled 1.29. From Fig. 7 and Table 1 it follows that the dissolution of steel from the completely active state is mainly controlled by diffusion. The increase in the temperature coefficients (Table 1) with a decrease in the corrosion rate below $k_{a.s.}$, which occurs when the potential is moved toward positive or negative values from $\varphi_{a.s.}$ (Fig. 7), indicates elimination of diffusion retardation of steel solution. From the similarity of the temperature coefficients of the corrosion rates of completely active steel in 3% nitric acid ($\frac{k_{20^\circ}}{k_{10^\circ}} = 1,29$) and of diffusion of 3% nitric acid ($\frac{D_{20^\circ}}{D_{10^\circ}} = 1,31$) [14] it may obviously be considered that the corrosion of active stainless steel in nitric acid is mainly controlled by diffusion due to the slow supply of nitric acid to the steel surface. In this connection, it was to be expected that an increase in the nitric acid concentration should lead to a removal of diffusion retardation of activated stainless steel solution. The increase in the temperature coefficients of the corrosion rate at a constant potential with an increase in the nitric acid concentration confirms this hypothesis (Table 2).

The conclusion that there is diffusion retardation of activated stainless steel solution in dilute nitric acid solutions is also confirmed by data on the effect of stirring the acid on the corrosion behavior of stainless steels (Fig. 2, curves 3 and 3a). As was to be expected, stirring the acid, which leads to acceleration of the supply of acid to the steel surface, considerably increases the corrosion rate of activated stainless steel.

SUMMARY

1. A study was made of the characteristics of dissolution of stainless steels in nitric acid solutions during cathodic polarization in relation to potential, acid concentration, and temperature.
2. The dissolution of stainless steels during cathodic polarization in nitric acid solutions is retarded by diffusion due to the slowness of the supply of acid to the steel surface.

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*Original Russian pagination. See C. B. translation.

THEORY OF CHAIN-THERMAL FLAME PROPAGATION

COMMUNICATION 1. TWO ACTIVE CENTERS

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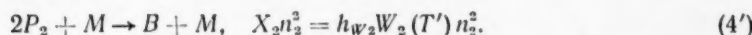
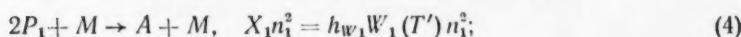
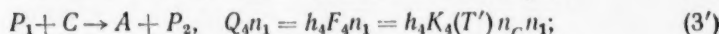
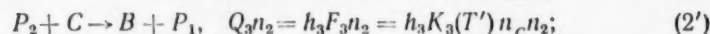
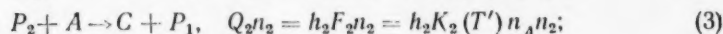
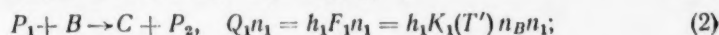
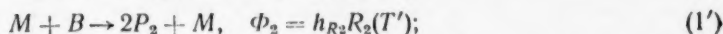
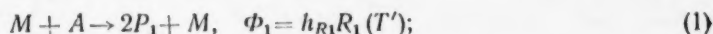
Translation from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 6, pp. 1022-1029, June, 1960

Original article submitted November 25, 1958

On the basis of results obtained in previous work [1, 2] in which the chain mechanism of the decomposition reaction was represented by a simplified scheme with an active center of one type, in the present work we deduce relations for determining the flame propagation rate in a system with two active centers.

Reaction scheme and system of equations. We adopted the following form of reaction scheme, in which A and B are the starting materials, C is the final reaction product, and P_1 and P_2 are the active centers:



The expressions for the heat evolution rate are written at the right-hand side. Here h_i is the heat effect of the reaction (in kcal/mole), n_1 and n_2 are the concentrations of active centers P_1 and P_2 (in mole/g of mixture), n_A , n_B , and n_C are the concentrations of substances A, B, and C (in mole/g of mixture), K_i and W_i are the reaction rate constants (in $g^2/cc \cdot mole \cdot sec$), R_i is the chain initiation rate (mole/cc $\cdot sec$), and T' is the temperature in $^{\circ}K$. It is assumed that the diffusion coefficients of the starting materials D_A and D_B and of the reaction product D_C equal to thermal conductivity coefficient ($\lambda = c\rho D_A = c\rho D_B = c\rho D_C$) and therefore the rates of chain initiation (1) and (1') and also the expression for F_i are written as functions of temperature alone.

The system of equations describing the process of stationary propagation of a flat laminar flame for the reaction scheme presented and the conditions adopted reduces to three equations:

$$\lambda\rho \frac{dp}{dT} - Bcp + Q_1n_1 + Q_2n_2 + Q_3n_2 + Q_4n_1 + \sum X_i n_i^2 + \sum \Phi_i = 0, \quad (5)$$

$$D \frac{d^2n_1}{dx^2} - B \frac{dn_1}{dx} + F_2n_2 + F_3n_2 - F_1n_1 - F_4n_1 + R_1 - W_1n_1^2 = 0, \quad (6)$$

$$D \frac{dn_2}{dx^2} - B \frac{dn_2}{dx} + F_1 n_1 + F_4 n_1 - F_2 n_2 - F_3 n_2 + R_2 - W_2 n_2^2 = 0, \quad (7)$$

$$\text{where } B = u\rho, \quad D = \rho D_{p1} = \rho D_{p2}, \quad T = T' - T_0, \quad \sum_i X_i n_i^2 = X_1 n_1^2 + X_2 n_2^2,$$

$$\sum \phi_i = \phi_1 + \phi_2 \text{ and } p = \frac{dT}{dx},$$

where x is the coordinate on the axis normal to the flame surface (in cm), u is the flow rate along the x axis (in cm/sec), ρ is the density (in g/cc), λ is the thermal conductivity of the mixture (in cal/cm·sec·deg), c is the heat capacity at constant pressure (in cal/g·deg), and D_{p1} and D_{p2} are the diffusion coefficients of the active centers (in cm²/sec). The index "0" refers to the initial state of the fresh mixture ($T' = T_0$), the index "1" refers to the state at the combustion temperature ($T' = T_1$), and the index "m" refers to the state corresponding to the maximum temperature gradient ($T' = T_m$). The extreme values of the functions of the rates of the chemical reactions equal zero [1, 2], while the limiting conditions for equations (5-7) are similar to those presented in [1].

Determination of flame propagation rate. A relation for determining the flame propagation rate with allowance for the rate of chain initiation and the rate of quadratic chain termination with a simplified scheme for the chain reaction was obtained in [2]. On numerical examples in [2] it was established that allowance for the rates of chain initiation and quadratic termination has very little effect on the calculated flame propagation rate since the concentration of the active center in the reaction zone is determined mainly by its diffusion from regions with a high concentration in systems with unbranched reactions or in cases where the rate of the branching process is much less than the rate of the chain propagation process. Therefore, to simplify the results of the present examination, it will first be assumed that $R_1 = R_2 = 0$ and $W_1 = W_2 = 0$. We will later show how the propagation rate is calculated with allowance for the initiation rate ($R_1 \neq 0$) and quadratic chain termination ($W_1 \neq 0$) by means of the approximate relations obtained in [2].

The method of solving the given problem, which is based on the representation of the solutions of equations of type (6) and (7) in the form of second-order polynomials, is given in detail in [1], where this approximate method was checked by comparison with the results of a numerical integration of the initial system of equations. According to [1] and on the basis of (5-7), the concentrations of active centers at the temperature $T = T_m$, corresponding to the maximum temperature gradient $p = p_m$, are represented in the form

$$n_{1m} = t_1 + (G_{2m} n_{2m} - G_{1m} n_{1m} - B l_1 p_m) N, \quad (8)$$

$$n_{2m} = t_2 + (G_{1m} n_{1m} - G_{2m} n_{2m} - B l_2 p_m) N, \quad (9)$$

$$\text{where } G_1 = F_1 + F_4, \quad G_2 = F_2 + F_3, \quad l_1 = \frac{n_{1r} - n_{10}}{T_r}, \quad l_2 = \frac{n_{2r} - n_{20}}{T_r},$$

$$N = \frac{r}{2D_m p_m^2}, \quad t_1 = n_{10} + l_1 T_m, \quad t_2 = n_{20} + l_2 T_m,$$

$$r = T_m (T_r - T_m), \quad T_m = 0.5 T_r.$$

By combining (8) and (9), we find the total concentration of active centers when $T = T_m$

$$n_m = n_{1m} + n_{2m} = t - B l p_m N, \quad (10)$$

where $t = t_1 + t_2$ and $l = l_1 + l_2$.

By solving (8) and (9) with allowance for (10), we obtain the final expressions for the concentrations of active centers at $T = T_m$

$$n_{1m} = \frac{t_1 + G_{2m}Nn_m - Bl_1p_mN}{1 + (G_{1m} + G_{2m})N}, \quad (11)$$

$$n_{2m} = \frac{t_2 + G_{1m}Nn_m - Bl_2p_mN}{1 + (G_{1m} + G_{2m})N}. \quad (12)$$

Now, for the over-all rate of heat evolution $Q_m n_m = S_{1m}n_{1m} + S_{2m}n_{2m}$, which is present in equation (5), by substituting (11) and (12) we obtain (when $R_1 = R_2 = 0$ and $W_1 = W_2 = 0$)

$$Q_m n_m = \frac{S_{1m}(t_1 + G_{2m}Nn_m - Bl_1p_mN) + S_{2m}(t_2 + G_{1m}Nn_m - Bl_2p_mN)}{1 + (G_{1m} + G_{2m})N}, \quad (13)$$

where $S_1 = Q_1 + Q_4$ and $S_2 = Q_2 + Q_3$.

By substituting n_m from (10) in (13), after rearrangement we find

$$Q_m = \frac{(l_1 S_{1m} + l_2 S_{2m}) + (S_{1m} G_{2m} + S_{2m} G_{1m}) N l}{l(1 + G_{1m} N + G_{2m} N)}. \quad (14)$$

By determining the over-all concentration of active centers n_m by (10) and the over-all value Q_m by (14), determination of flame propagation with two active centers is reduced to the solution obtained in previous work [1-3] for the simplified scheme of the chain reaction with an active center of one type. This confirms the applicability of the simplified scheme used previously.

The following relation for the maximum temperature gradient $p_m = p_*$ was obtained in [3]:

$$p_m^2 = Q_m \frac{r}{2D_m} L, \quad (15)$$

$$\text{where } L = \frac{l}{c} \frac{(x-2q)}{2q}, \quad q = \frac{\mu_0}{\mu_m} \left(\frac{T_0}{T_m} \right)^{a-1} \quad \text{or} \quad D_p \sim (T')^a \quad \text{and} \quad x = \frac{cD_0}{\lambda_0}.$$

By substituting (15) in (14) and considering the symbols adopted in (8) and (9), we find from the quadratic equation

$$Q_m = \frac{(LQ_l - G_m) \pm \sqrt{(LQ_l - G_m)^2 + 4LQ_G}}{2L}, \quad (16)$$

$$Q_l = \frac{l_1 S_{1m} + l_2 S_{2m}}{l},$$

$$Q_G = S_{1m}G_{2m} + S_{2m}G_{1m} \text{ and } G_m = G_{1m} + G_{2m}.$$

By neglecting LQ_l in comparison with G_m , i.e., considering that $LQ_l \ll G_m$ (this is practically always the case), and expanding the radical in (16) into a series, we obtain an approximate relation for Q_m , which will give a value that practically coincides with Q_m calculated from relation (16):

$$Q_m \approx \frac{Q_G}{G_m} = \frac{(Q_{1m} + Q_{4m})(F_{2m} + F_{3m}) + (Q_{2m} + Q_{3m})(F_{1m} + F_{4m})}{F_{1m} + F_{2m} + F_{3m} + F_{4m}}. \quad (17)$$

Assuming that the rates of processes parallel to processes (2) and (3) equal zero (or are negligibly small: $F_4 \ll F_1$ and $F_3 \ll F_2$), i.e., considering that $F_4 = 0$ and $F_3 = 0$ (or $F_4 \approx 0$ and $F_3 \approx 0$), we obtain from (17) a simpler relation for the determination of Q_m under these conditions:

$$Q_m = (h_1 + h_2) \frac{F_{1m} F_{2m}}{F_{1m} + F_{2m}}. \quad (18)$$

Finally, in accordance with [3] we find the following known relation for determining the flame propagation rate u_0 :

$$u_0 = \varphi \frac{1}{\rho_0} \sqrt{\frac{n_r Q_m \rho_m D_{pm}}{2cT_r}}, \quad (19)$$

$$\text{where } \varphi = 2 \sqrt{\frac{2q}{\alpha} \left(1 - \frac{2q}{\alpha}\right)}, \quad n_r = n_{1r} + n_{2r},$$

$D_p = D_{p_1} = D_{p_2}$, while Q_m is determined from (16), (17), or (18).

Assuming, as in [1], that the distribution of the concentrations of P_1 and P_2 is determined by the values at $T = T_m$, from (11) and (12) we obtain temperature dependencies of the concentrations of active centers:

$$n_1(T) = \frac{(2D_m \rho_m^2 l_1) T + (G_{2m} n_m - \gamma l_1 \rho_m^2) T (T_r - T)}{2D_m \rho_m^2 + (G_{1m} + G_{2m}) T (T_r - T)}, \quad (20)$$

$$n_2(T) = \frac{(2D_m \rho_m^2 l_2) T + (G_{1m} n_m - \gamma l_2 \rho_m^2) T (T_r - T)}{2D_m \rho_m^2 + (G_{1m} + G_{2m}) T (T_r - T)}, \quad (21)$$

where $n_m = \frac{n_r}{2} \left(1 - \frac{2q}{\alpha}\right)$, $\gamma = 4D_m q \frac{1}{\alpha T_m}$, and p_m is found from (15).

In accordance with (2), (2'), (3), and (3'), $h_1 = -h_4$ and $h_2 = -h_3$. However, in relations of this section for Q_m , the heat effects, which are equal in absolute value, are not taken out of the brackets as in the general case, processes (2') and (3'), which lead to the formation of P_1 and P_2 , respectively, may not be the exact reverse of processes (2) and (3), but will lead to the formation of some other products instead of B and A. In this case, their heat effects and those of (2) and (3) will not be equal in absolute value.

Allowance for the rates of chain initiation and quadratic termination. For determining the rate of flame propagation with allowance for the rate of chain initiation, in [3] we obtained an approximate relation in the form of a rate coefficient ξ (with the symbols and dimensions as in [3], but marked with dashes as they differ from those adopted in the present article):

$$\xi = \sqrt{\frac{1}{2} (1 + \sqrt{1 + M})}, \quad (22)$$

$$\text{where } M = \frac{32qx}{(\alpha - 2q)^2} \frac{R'_m}{K'_m (n'_r)^2}.$$

In accordance with [3] and the results and symbols of the present investigation [see (10) and (19)], it is obvious that $R'_m = \mu' (R_{1m} + R_{2m})$, $n'_r = \mu' (n_{1r} + n_{2r})$ and $K'_m = 2Q_m / \mu' c T_r$. By substituting these relations in (22), we find ξ in the symbols of the present article:

$$\xi = \sqrt{\frac{1}{2} \left(1 + \sqrt{\frac{16qxcT_r}{(\alpha - 2q)^2 n_r^2 Q_m} (R_{1m} + R_{2m})}\right)} \quad (23)$$

A relation for the determination of the flame propagation rate with allowance for the rate of quadratic chain termination was obtained in [2]. Due to the complexity of this relation, here we will use the simple approximate relation obtained in the same article in the form of the rate coefficient ψ , the applicability of which was based on numerical examples in [2]. For the present case (with the symbols and dimensions in [2]), we obtain the following relation from [2] after simplification:

$$\psi = \left(1 + \frac{2q}{\alpha} \frac{W'_m}{K'_m}\right)^{-\frac{1}{2}} \quad (24)$$

In accordance with [2] and the present conditions, by substituting $W'_m = (W_{1m} + W_{2m})/\mu'$ and $K'_m = 2Q_m/\mu'cT_\Gamma$ in (24), we find a relation for ψ in the symbols of the present article:

$$\psi = \left[1 + \frac{qcT_\Gamma}{\alpha Q_m} (W_{1m} + W_{2m})\right]^{-\frac{1}{2}} \quad (24)$$

Relation for determining flame propagation rate with allowance for all processes. Now, on the basis of the results obtained in previous sections, we may write the final expression for determining the flame propagation rate corresponding to the initial system of equations (5-7) and considering all the processes given by (1), (1'), (2), (2'), (3), (3'), (4) and (4'):

$$u_0 = \varphi \dot{\psi} \frac{1}{\rho_0} \sqrt{\frac{n_\Gamma Q_m \rho_m D_{pm}}{2cT_\Gamma}}, \quad (26)$$

where φ , n_Γ , and D_p are found from the relations with (19), ξ from (23), ψ from (25), and Q_m is determined from (16), (17), or (18).

From relations (23) and (25) it follows that when $R_{1m} = R_{2m} = 0$, the coefficient $\xi = 1$ and when $W_{1m} = W_{2m} = 0$, the coefficient $\psi = 1$. In this case relation (26) changes into the simpler relation (19). The effect of the rate of chain initiation on the value of u_0 under otherwise equal conditions depends on the ratio $(R_{1m} + R_{2m})/Q_m$ as an increase (or decrease) in the rate of heat evolution, which leads to a rise (or fall) in the temperature and concentration gradients, increases (or decreases) the amount of active centers supplied by diffusion at $T = T_m$, which leads to a decrease (or increase) in the role of the rate of chain initiation. Therefore, an increase in Q_m leads to a decrease in the effects of the rate of quadratic chain termination on the flame propagation rate.

The suitability of the value of Q_m from (18) (when $F_4 < F_1$ and $F_3 < F_2$) in comparison with the more accurate value of Q_m from (17) for use in relation (26) depends on the accuracy required for the calculation results and the values of F_4 and F_3 in comparison with F_1 and F_2 and is readily estimated from relation (17).

DISCUSSION OF RESULTS OBTAINED

In the previous examination of flame propagation [1-3], the mechanism of the successive (unbranched) chain reaction was represented by a simplified scheme with an active center of one type. Relations (17) and (10) make it possible to determine for this simplified scheme [1, 2] the effective rate constant of the chain propagation process and the effective concentration of the active center of one type from data for a reaction scheme with two active centers.

From an examination of relation (18) it follows that the value of Q_m , on which depends the rate of heat liberation in (19) and consequently, the rate of flame propagation, is determined mainly by the least of the values F_{1m} or F_{2m} . The value of Q_m is independent of $n_{1\Gamma}$ and $n_{2\Gamma}$ and the separate heat effects h_1 and h_2 , but is determined by the algebraic sum of the heat effects of the two successive processes responsible for chain propagation. If, for example, $F_{1m} < F_{2m}$, then $Q_m \approx (h_1 + h_2) E_{1m}$ (when $F_{1m} = F_{2m}$, $Q_m = (h_1 + h_2) F_{1m}/2 = (h_1 + h_2) F_{2m}/2$). Therefore, an effect on the value of u_0 when $G_{1m} < G_{2m}$ [according to relation (17)] may be produced, under otherwise equal conditions, only by a change in the least value of $G_{1m} = F_{1m} + F_{4m}$, as even a considerable change in $G_{2m} = F_{2m} + F_{3m}$ will not have an appreciable effect on the flame propagation rate until $G_{1m} < G_{2m}$. The heat evolution rate also depends on $n_\Gamma = n_{1\Gamma} + n_{2\Gamma}$, which is determined mainly by the greatest of the concentrations of the two active centers at the combustion temperature. As follows from relation (19), it is essential that the greatest concentration is determined from a comparison of the concentrations in moles per gram of mixture or the partial pressures, which are proportional to them. The active center with the greatest partial pressure at the combustion temperature will be the determining (driving) active center.

In [4] we investigated the effect of pressure and temperature on the flame propagation rate according to the relation obtained for the simplified reaction scheme [1]. The effect of allowance for chain branching and termination on the pressure dependence of u_0 was examined qualitatively in [2]. The dependence of u_0 on pressure and combustion temperature T_Γ is determined mainly by the change in concentration of active centers with pressure and temperature. In [4], it was assumed that for hydrocarbon-air and hydrocarbon-oxygen combustion mixtures, the determining (driving) center is one of several active centers, which participate successively in the combustion chain reaction. Relation (19) makes it possible to estimate quantitatively the driving role of one of two active centers with identical diffusion coefficients. In the reaction scheme adopted in the present article, the driving active center will be the one whose partial pressure at the combustion temperature is greatest. If, for example, $n_{1\Gamma} = 10 \cdot n_{2\Gamma}$, then calculation of the pressure dependence of u_0 from a relation of the type (19) with allowance for the change only in $n_{1\Gamma}$ (i.e., assuming that $n_{2\Gamma} \approx 0$) leads to an error in u_0 of not more than 5%. With approximately equal values of $n_{1\Gamma}$ and $n_{2\Gamma}$, the dependence of u_0 on the pressure P_Σ will be intermediate between the two cases for which $u_0(P_\Sigma)$ is calculated only from $n_{1\Gamma}$ or only from $n_{2\Gamma}$. The concentration of the different active centers may depend differently on pressure for a given mixture. With a change in the initial composition of the mixture, the rate of change of concentration of a given active center changes. These characteristics are shown on graphs in [4] for ethylene-air mixtures of various compositions. Therefore, with a decrease in pressure, the leading role (in the above sense) may pass from one active center to another, whose concentration increases more rapidly with a fall in pressure.

The relation of u_0 to combustion temperature T'_Γ is determined to a considerable extent by the change in the concentration of active centers with T'_Γ . The slope of the graph of the experimental relation in the coordinates $\log u_0$ - reciprocal temperature depends largely on the heat of formation of the active center [4]. Therefore, in the analysis of experimental data by means of formulas obtained without allowance for diffusion of the active center, instead of the activation energy E , we find some effective value $E_\phi = H_1 + E$, where H_1 is the effective heat, which depends on the initial composition of the combustion mixture and is determined by the proportionality ratio $\sqrt{n_{iv}} \sim \exp(-H_1/RT'_\Gamma)$.

Relation (19) makes it possible to determine the constants and activation energies of processes (2) and (3) from the experimental relations of u_0 and T'_Γ when $F_3 = F_4 = 0$. If, for example, in mixtures with excess of substance B, $F_{1m} > F_{2m}$, then from relation (18) it follows that $Q_m \approx (h_1 + h_2) F_{2m}$ and it is possible to determine the constant and activation energy of process (3). If, however, in mixtures with excess A $F_{1m} < F_{2m}$ or $Q_m \approx (h_1 + h_2) F_{1m}$, it is possible to find the constant and activation energy of process (2). Having determined the constant and activation energy of process (3), for example, we can readily find the constant and activation energy of process (2) from the relation of u_0 to T'_Γ in mixtures with excess A. When the constant and activation energy of either process (2) or (3) are known, then the constant and activation energy of the second process is determined from relations (18) and (19) at any values of F_{1m} and F_{2m} if the experimental relation of u_0 and T'_Γ is known. The relation of $n_\Gamma = n_{1\Gamma} + n_{2\Gamma}$ to combustion temperature, which is needed to find the experimental values of the constants and activation energies of processes (2) and (3), is calculated from the corresponding equilibrium constants.

The distribution of active center concentrations in relation to the change in temperature is given by relations (20) and (21). If, for example $n_{1\Gamma} > n_{2\Gamma}$, then the driving active center will be P_1 and the total concentration of active centers at the temperature $T = T_m$, corresponding to the maximum temperature gradient, will be determined mainly by the diffusion of P_1 , while the relation $n(T) = n_1(T) + n_2(T)$ will have the form of a curve, rising continuously from the initial concentration $n = n_0$ to the final one $n = n_\Gamma$, which is the greatest from the initial temperature to the combustion temperature. The relation $n_1(T)$ will be a curve of the same nature, while the curve of the relation $n_2(T)$ will have a maximum between the initial temperature and the combustion temperature as, at a relatively low value of l_2 , the value of the numerator in relation (21) will be determined mainly by the dependence $F_{1m} n_m T (T_\Gamma - T)$. With the unbranched reaction scheme adopted in the present article and actual values of chain generation rates, both curves of $n_1(T)$ and $n_2(T)$ cannot simultaneously have maxima in the reaction zone.

Numerical calculations. Relation (26) obtained makes it possible to calculate absolute theoretical values of the rates of flame propagation for actual cases by using experimental (using independent, purely kinetic methods) rate constants and activation energies of the elementary processes, required for the calculation. The chain reaction scheme presented at the beginning of the article applies to the combustion of chlorine-hydrogen mixtures.

Experimental and Theoretical Flame Propagation Rates (in cm/sec) for Chlorine - Hydrogen Mixtures

Composition of combustion mixture	0,6H ₂ +0,4Cl ₂	0,5H ₂ +0,5Cl ₂
Experimental data of Bartolome [5]	405	350
From relation (26).	350	485

For two cases of chlorine-hydrogen mixtures, we used relation (26) to calculate the flame propagation rates, which are given in the table together with the corresponding experimental values from Bartolome's data [5]. The rate constants of processes (2) and (3) were taken from [6]:

$$K_1 = 10^{13,9} \rho^2 \exp\left(-\frac{5500}{RT}\right),$$

$$K_2 = 10^{13,4} \rho^2 \exp\left(-\frac{2500}{RT}\right)$$

(it was assumed that $K_3 = 0$ and $K_4 = 0$). The transfer coefficients were taken from [7]: $(D_{P_1})_0 = 0.19$ (Cl atom), $(D_{P_2})_0 = 1.04$ (H atom), and $\lambda_0 = 8.6 \cdot 10^{-5}$. In the derivation of relation (26) it was assumed that the two active centers have the same diffusion coefficients. Therefore, for the hydrogen-chlorine mixture it was necessary to determine some effective value of the diffusion coefficient for hydrogen and chlorine atoms. Since the rate of flame propagation in a system with an unbranched reaction is determined by the diffusion flow of active centers, the effective value of the diffusion coefficient for relation (26) was calculated from the relation $D_{Pm} = (D_{P1}n_{P1} + D_{P2}n_{P2}) / (n_{P1} + n_{P2})$. In the next article we will publish a solution for the case when $D_{P1} \neq D_{P2}$. For the initial compositions of the combustion mixtures presented in the table, $\xi = 1.00$ and $\psi = 1.00$, though the greatest possible value was adopted for the rate constant of chlorine atom formation.

Considering the comparison of the theoretical values of u_0 , calculated from a relation of the type (26), with the results of numerical integration of the initial system of equations for an active center of one form, presented in [1], and also the agreement between the experimental and theoretical values in the table, it may be concluded that the theoretical examination of flame propagation in systems with unbranched chain reactions accurately describes the actual propagation of such a flame.

SUMMARY

1. For a chain reaction scheme with two active centers, successively reacting with the starting materials and regenerating each other, we obtained a relation for determining the flame propagation rate with allowance for diffusion of both active centers and also with allowance for the rates of chain initiation and quadratic termination.
2. The theoretical flame propagation rates were calculated for two cases of the combustion of chlorine-hydrogen mixtures and these agreed satisfactorily with experimental data.
3. A qualitative examination was made of the relations of flame propagation rate to pressure and combustion temperature, which were derived from the solution with allowance for the diffusion of two active centers, in comparison with results obtained by an examination of the simplified scheme with an active center of one type.

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SYNTHESIS OF PHOSPHONIC ESTERS
CONTAINING HETEROCYCLIC GROUPS

COMMUNICATION 6. REACTION OF PHOSPHOROUS ESTERS

WITH 2-FURALDEHYDE, 2-FUROIC ACID, AND 2-FURANACRYLIC ACID

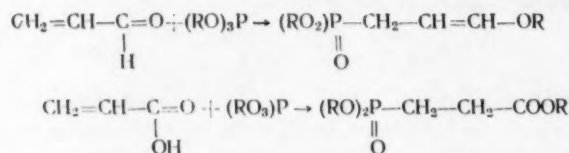
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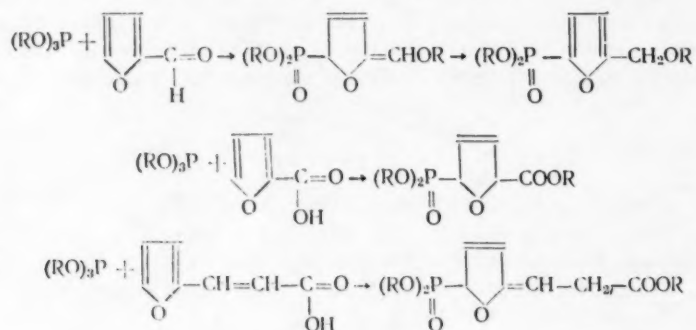
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 6, pp. 1030-1034, June, 1960

Original article submitted October 12, 1958

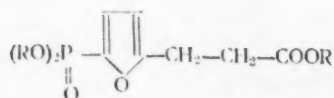
Kamai and Kukhtin showed [1] that phosphorous triesters add to α, β -unsaturated aldehydes and α, β -unsaturated acids with formation of phosphonic esters:



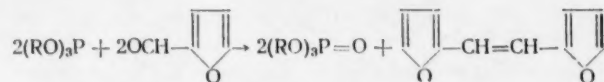
It may be supposed that conjugated systems containing many double bonds will also be capable of this sort of addition reaction. Such systems are found in the aldehydes and acids of the furan series. When trialkyl phosphites add to these we should obtain substituted furyl- or dihydrofuryl-phosphonic esters:



or

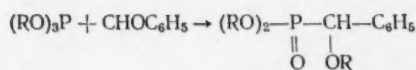


When these reactions were carried out it was found that the actual process occurring was more complex. Only in the case of 2-furanacrylic did we isolate a reaction product corresponding to the above scheme. When triethyl or triisopropyl phosphite was heated with 2-furaldehyde at 160°, the phosphorous ester was oxidized to the phosphoric ester at the expense of the oxygen of the aldehyde group. From the reaction products we isolated 2, 2'-vinylenedifuran, m.p. 100-101°, in small amounts:



Hence, a trialkyl phosphite behaves as an oxygen acceptor and reacts by abstraction of oxygen from the aldehyde group.

To determine the possibility of the occurrence of this reaction with other aldehydes we carried out experiments on the reaction of triethyl and tripropyl phosphites with benzaldehyde under severe conditions. In this case also, apart from the product of the addition of the trialkyl phosphite to the aldehyde group by the reaction described by Abramov [2]



we obtained the trialkyl phosphate and small amounts of stilbene, m.p. 124-125°.

The reaction of oxygen abstraction by phosphite described in the present paper has an analogy in the abstraction of sulfur from thiols and disulfides by phosphites, as has been found previously [3, 4].

When triethyl or triisopropyl phosphite was heated with 2-furoic acid to 130-160°, from the reaction products we isolated ethyl or isopropyl 2-furoate, respectively, which is analogous to the esterification of carboxylic acids with a dialkyl hydrogen phosphite [5].

The reaction between triethyl phosphite and 2-furanacrylic acid is complex. From the reaction products we isolated diethyl hydrogen phosphite, ethyl 2-furanacrylate, and a product having: b.p. 157-158° (3 mm); n_D^{20} 1.4820; d_4^{20} 1.1709; MR74.05. In analysis this substance corresponded to the product of the addition of triethyl phosphite to 2-furanacrylic acid. The structure of the product was not finally established.

EXPERIMENTAL

Reaction of Triethyl Phosphite with 2-Furaldehyde. A mixture of 10.5 g of triethyl phosphite and 6.1 g of freshly distilled 2-furaldehyde was heated in an Arbuzov flask at 160° for three hours. The mixture, which was at first colorless, began to turn brown at about 140° and finally became very dark in color. Vacuum fractionation gave: Fraction I; b.p. 54-63° (3 mm); 3.5g; n_D^{20} 1.4810; Fraction II; b.p. 63-85° (3 mm); 7.7 g; n_D^{20} 1.4450; and a solid resinous residue.

Redistillation through a column of eight-plate efficiency gave 2.7 g of a product having: b.p. 78.5-80° (4.5-5 mm); 2.7 g; n_D^{20} 1.4095; d_4^{20} 1.0723. It corresponded in analysis to triethyl phosphate. Found: P 16.71%. $\text{C}_8\text{H}_{15}\text{O}_4\text{P}$. Calculated: P 17.01%. The literature gives: b.p. 99.2° (13 mm); d_4^{20} 1.0681; n_D^{20} 1.4061. From the fraction which followed after triethyl phosphate we isolated needles of m.p. about 101-102°; it was phosphorus-free. A mixture with 2,2'-vinylenedifuran isolated in the experiment with triisopropyl phosphite melted without depression.

Reaction of Triisopropyl Phosphite with 2-Furaldehyde. The experiment was carried out with larger amounts of reactants than in the first case. A mixture of 21.5 g of triisopropyl phosphite and 10 g of 2-furaldehyde was heated at 160-165° (in mixture) for five hours. We obtained a thick dark-brown liquid. Two distillations gave 11 g (about 50%) of a product having b.p. 87.5-88.5° (5 mm) (through a column of eight-plate efficiency); n_D^{20} 1.4062; d_4^{20} 0.9876; Found: MR 55.77; Calculated: MR 55.75. For triisopropyl phosphate the literature gives: b.p. 105° (13 mm); d_4^{20} 0.9851; n_D^{20} 1.4066. From the higher fractions we isolated a small amount of crystalline substance, m.p. 100-101° (from ethanol). Found: C 74.76; H 5.04%; no phosphorus. $\text{C}_{10}\text{H}_{18}\text{O}_2$. Calculated C 75.00; H 5.03%.

Reaction of Triethyl Phosphite with 2-Furoic Acid. An Arbuzov flask was charged with 4.58 g of 2-furoic acid and 10 ml of dry benzene. One half of the benzene was distilled off to remove traces of water from the 2-furoic acid. To the suspension that remained we added 6.8 g of triethyl phosphite (1 mole per mole of acid). The mixture was heated at 130-140° for three hours. After several distillations we isolated 2 g of a fraction of b.p. 53-58° (3 mm); d_4^{20} 1.0782; n_D^{20} 1.4175. The literature gives: b.p. 76° (14 mm); d_4^{20} 1.0756; n_D^{20} 1.4080. In analysis the fraction isolated corresponded to impure diethyl hydrogen phosphite, probably contaminated with ethyl 2-furoate. This view was confirmed by the fact that from the next fraction (b.p. 58-64° at 3 mm) we isolated 0.6 g of crystals, m.p. 35-47° (washed with petroleum ether). For ethyl 2-furoate the literature gives: m.p. 34-35°; b.p. 195°; n_D^{20} 1.4797. As will be seen from the data cited, the boiling points of diethyl hydrogen phosphite and ethyl 2-furoate are very close together.

Reaction of Triisopropyl Phosphite with 2-Furoic Acid. A mixture of 20.8 g of triisopropyl phosphite and 11.2 g of 2-furoic acid (m.p. 130-131°) was heated in an Arbuzov flask at 150-160° for three hours. The contents of the flask formed a clear dark-yellow liquid. Distillation gave three fractions: Fraction I (2.5 g), b.p. 80-87° (15-13 mm) and n_D^{20} 1.4292; Fraction II (23.1 g), b.p. 87-115° (14-13 mm) and n_D^{20} 1.4390; and Fraction III, b.p. 115-135° (13 mm). From Fraction III we isolated about 3 g of 2-furoic acid (m.p. 125-129°); the residue was a small amount of resin. Fraction II was fractionated through the eight-plate column. Several fractions were obtained: Fraction I (5.5 g), b.p. 63-68° (4 mm); n_D^{20} 1.4095; d_4^{20} 0.9999; Found: P 18.32; $C_6H_{15}O_3P$; Calculated: P 18.66%; for diisopropyl hydrogen phosphite the literature gives: b.p. 80.5° (12 mm); n_D^{20} 1.4090; d_4^{20} 0.9962. Fraction II (3 g), b.p. 68-79° (4 mm) and n_D^{20} 1.4100. Fraction III (0.5 g), b.p. 79-83° (4 mm) and n_D^{20} 1.4212. Fraction IV (3.2 g), b.p. 83-88° (4 mm) and n_D^{20} 1.4498. Fraction V (7.7 g), b.p. 88-92° (4 mm); n_D^{20} 1.4645; d_4^{20} 1.0602. For isopropyl 2-furoate the literature gives: b.p. 198.6°, n_D^{23} 1.4682; d_4^{23} 1.0655. The residue amounted to 1.5 g.

Reaction of Triethyl Phosphite with 2-Furanacrylic Acid. A mixture of 21 g of 2-furanacrylic acid [m.p. 141° (from benzene)] and 25.3 g of triethyl phosphite was placed in an Arbuzov flask fitted with a thermometer reaching almost to the bottom and heated in an oil bath. At a bath temperature of about 130-135° the contents of the flask melted (temperature in mixture 110°). The temperature of the mixture was rapidly raised to 149° and was kept at this level for some time. The mixture was further heated at 150-160° for three hours. A reddish-orange liquid was obtained. Distillation from an Arbuzov flask gave several fractions:

Fraction I (0.5 g), b.p. 45-62° (16 mm) and n_D^{20} 1.4115. Fraction II (9.5 g), b.p. 69-92° (16 mm) and n_D^{20} 1.4245 (this mainly distilled at 79-92° at 6.5 mm). Fraction III (2.5 g), b.p. 92-96° (6.5 mm) and n_D^{20} 1.4860. Fraction IV (6.8 g), b.p. 90-110° (3 mm) and n_D^{20} 1.5280. Fraction V (1.5 g), b.p. 110-130° (3 mm) and n_D^{20} 1.5340.

With further heating of the bath to 200-210° the residual pressure rose to 6 mm; a little decomposition set in, but a pressure of 3 mm was quickly restored. Fraction VI (19.3 g) had b.p. 173-175° (3 mm) and n_D^{20} 1.4820. The residue (about 5.5 g) was a thick dark-colored liquid.

Fraction VI was redistilled from an Arbuzov flask with a low side-tube; we then isolated 14 g of a product having b.p. 157-158° (3 mm); n_D^{20} 1.4820; d_4^{20} 1.1709; Found: MR 74.05; Calculated MR 73.26. When allowed to stand, the thick oily liquid became brown. Found: C 52.5; H 6.70; P 9.1%. $C_{13}H_{21}O_6P$. Calculated: C 51.28; H 6.95; P 10.19%.

On refractionation of Fractions II-V we isolated two more products: the first (3.5 g) had b.p. 54-56° (3.5 mm); n_D^{20} 1.4082; d_4^{20} 1.0747 (for diethyl hydrogen phosphite the literature gives n_D^{20} 1.4080; d_4^{20} 1.0756); the second (5.2 g) had b.p. 100-101° (5 mm); n_D^{20} 1.5325; d_4^{20} 1.0927 (for ethyl 2-furanacrylate the literature gives: b.p. 117° (8 mm); n_D^{20} 1.5286; d_4^{25} 1.0891).

Hydrolysis of the latter with 10% barium hydroxide solution gave 2-furanacrylic acid, m.p. 138-140° (the literature gives m.p. 140-141°).

Reaction of Triethyl Phosphite with Benzaldehyde. A mixture of 16.6 g of triethyl phosphite and 10.6 g of benzaldehyde was heated in an Arbuzov flask at 160-170° for seven hours. Distillation gave the original reactants and 1.3 g of a product of b.p. 155-157° (6 mm). The reaction was considered to be incomplete. The mixture was sealed in a tube and heated at 220° for 8.5 hours. By repeated vacuum distillation of the reaction products we isolated 4 g of a product of b.p. 127-132° (2 mm); n_D^{20} 1.5043; d_4^{20} 1.1009; Found: MR 73.08; Calculated: MR 71.14. Found: C 59.45; H 7.51; P 11.45%. $C_{13}H_{21}O_4P$. Calculated: C 57.32; H 5.87; P 11.38%.

From the fractions close in boiling point to the above-described product [145-148° (6 mm)] 0.9 g of crystals of m.p. 124-125° (from alcohol) came down on standing. Found: C 93.20; H 6.80%; $C_{14}H_{12}$. Calculated: C 93.28; H 6.71%.

According to its analysis and melting point the substance was pure stilbene (m.p. 124°). The high carbon and hydrogen contents of the first product are probably to be explained by stilbene impurity.

Reaction of Tripropyl Phosphite with Benzaldehyde. A mixture of 21 g of tripropyl phosphite and 10.6 g of benzaldehyde was heated in a sealed tube at 200-210° for 4.5 hours. There was some decrease in the volume of the contents of the tube. The heating was continued at 200° for three hours; there was no further change in volume. Fractionation of the reaction products gave a large number of fractions, from which by repeated distillation we succeeded in isolating several products: Fraction I (5 g), b.p. 46-47° (7 mm) and n_D^{20} 1.5410 (for benzaldehyde the literature gives n_D^{20} 1.5450). Fraction II (5.5 g), b.p. 72-76° (6 mm) and n_D^{20} 1.4315 (strong phosphite odor; reacts with CuI). Fraction III (6 g); b.p. 118-119° (7.5-8 mm); n_D^{20} 1.4205; d_4^{20} 0.9870. Found: P 13.54%. $C_9H_{21}O_4P$. Calculated: P 13.87%. For tripropyl phosphate the literature gives: b.p. 120-121.5° (10 mm); n_D^{20} 1.4167; d_4^{20} 1.0118. Fraction IV (3.6 g); b.p. 138-140° (2.5 mm); n_D^{20} 1.5030; d_4^{20} 1.0602. Found: P 10.00, 10.09%. $C_{16}H_{27}O_3P$. Calculated: P 9.86%. Fraction V (2 g); b.p. 201-202° (3 mm); n_D^{20} 1.5110; d_4^{20} 1.1083 (the structure of the product was not determined); phosphorus content 11.47%.

SUMMARY

1. Triethyl and triisopropyl phosphites, when reacting with 2-furaldehyde and with benzaldehyde, are partially oxidized to phosphoric esters with formation of 2,2'-vinylenedifuran and stilbene, respectively.
2. When triethyl phosphite reacts with 2-furoic acid and with 2-furanacrylic acid, the ethyl esters of these acids are formed. In the case of 2-furanacrylic acid, not only the formation of a 2-furanacrylic ester occurs, but also the addition of the trialkyl phosphite to 2-furanacrylic acid.

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FLUORINE-CONTAINING β -SULTONES

COMMUNICATION 2. HYDROLYSIS OF

TETRAFLUORO-2-HYDROXYETHANESULFONIC ACID β -SULTONE

M. A. Dmitriev, G. A. Sokol'skii, and I. L. Knunyants

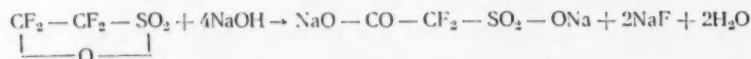
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No. 6, pp. 1035-1038, June, 1960

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It was previously reported [1] that the reaction of fluoro olefins with an equimolecular amount of sulfur trioxide (α -modification) leads to the formation of four-membered cycles, i.e., β -sultones. It was found that fluorine-containing β -sultones are extremely reactive compounds and react vigorously with various inorganic and organic substances. We now describe the products of the hydrolysis of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone and their reactions.

As already stated [1], in the alkaline hydrolysis of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone exactly four equivalents of alkali are consumed:



After being neutralized with alkali, a solution of the hydrolyzate of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone was evaporated down, and the neutral salt of difluorosulfoacetic acid was isolated.

The formation of a diacid in the hydrolysis of a β -sultone explains the isolation of chlorosulfoacetic acid and chlorosulfoacetaldehyde in the hydrolysis of the product formed by mixing fuming sulfuric acid with trichloroethylene [2] and 1,2-dichloroethylene [3], respectively. In these cases the intermediate products were undoubtedly of the sultone type and were hydrolyzed with opening of the lactone ring. On the basis of the fact that in the hydrolysis of the products of the reaction of dioxane - sulfur trioxide with allylbenzene [4], styrene [5], and 1-hexene [6] the corresponding 2-hydroxyalkanesulfonic acids were isolated, it must be considered that these reaction products were sultones. It may be supposed that, also in the case of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone, in the first stage of hydrolysis (action of one molecular proportion of water) opening of the lactone ring occurs. However, there was insufficient evidence to form a definite opinion on the structure of this product of incomplete hydrolysis.

On treatment of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone with an equimolecular amount of water, the liberation of one molecular proportion of hydrogen fluoride is observed and a stable readily distillable compound with the properties of a strong acid is formed. When this product is treated with aqueous alkali, exactly three equivalents of alkali are consumed and one equivalent of fluoride ions can be found in the solution. There can be no doubt that the product of the incomplete hydrolysis of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone is one of the two mono[acid fluorides] of the dibasic difluorosulfoacetic acid:



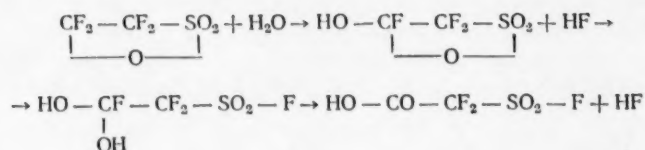
TABLE 1

Formula	B.p. (°C)	d_4^{20}	n_D^{20}	MR	
				found	calculated
F—SO ₂ —CF ₂ —CO—OH	153*	1,7234	1,3602	22,81	22,73
(F—SO ₂ —CF ₂ —CO) ₂ O	135—136	1,7441	1,3530	42,02	41,86
F—SO ₂ —CF ₂ —CO—Cl	67—68	1,6419	1,3570	26,15	26,14
F—SO ₂ —CF ₂ —CO—OCH ₃	115	1,5159	1,3510	27,38	27,47
F—SO ₂ —CF ₂ —CO—OC ₂ H ₅	129—130	1,3965	1,3565	31,60	32,08
F—SO ₂ —CF ₂ —CO—OC ₃ H _{7-i}	142—143	1,3478	1,3595	35,98	36,70

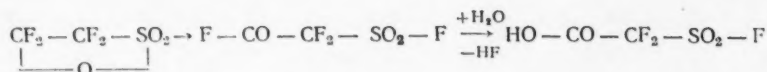
*B.p. 103° (95 mm).

The substance isolated is readily soluble in water and alcohols, and in neither case is the exchange of the fluorine of the acid fluoride group by hydroxyl or alkoxy observed. The hydrolysis of this compound with liberation of a fluoride ion occurs only with prolonged heating or in alkaline solutions. It is known, however, that acid fluorides of carboxylic acids are unstable to hydrolysis; their hydrolyzability is particularly increased by the introduction of electron-attracting atoms or groups of atoms in the α -position. On the other hand, acid fluorides of alkanesulfonic acids are relatively stable to hydrolysis [7]; the stability to hydrolysis of fully fluorinated alkanesulfonyl fluorides is particularly high [8]. Hence, of the two structures under consideration the second, i.e., that containing a sulfonyl chloride group and a carboxyl, describes the properties of the product isolated more fully.

The formation of difluoro(fluorosulfonyl)acetic acid in the hydrolysis of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone may be represented by several different schemes. In one of these schemes the first stage of the reaction is the hydrolytic cleavage of the β -fluorine-carbon bond, and the hydrogen fluoride liberated opens the sultone ring:



On the other hand it may be supposed that under the conditions of hydrolysis the cyclic β -sultone is isomerized into the linear bis[acid fluoride] of difluorosulfoacetic acid, which is then hydrolyzed to difluoro(fluorosulfonyl)acetic acid:



Like ordinary carboxylic acids, difluoro(fluorosulfonyl)acetic acid forms various derivatives. Thus, on treatment with phosphorus pentoxide the anhydride of the acid is formed in quantitative yield; treatment with phosphorus pentachloride gives the acid chloride; the acid chloride gives esters on treatment with alcohols. The physical properties of difluoro(fluorosulfonyl)acetic acid and some of its derivatives are given in Table 1.

EXPERIMENTAL

Difluorosulfoacetic Acid. A polytetrafluoroethylene reactor was charged with 25 ml of water, and 4.5 g of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone was added dropwise; much heat was evolved. The solution was evaporated on a steam bath until fluoride ions were absent in the residue. The residue (a sirupy liquid) was dissolved in 25 ml of water and neutralized to phenolphthalein with 1 N NaOH (about 48.5 ml). The neutralized aqueous solution was evaporated to dryness. The crystalline residue (5.3 g) was recrystallized from alcohol and washed with ether. The disodium salt of difluorosulfoacetic acid formed white needles which melted above 300°. The salt was readily soluble in water, of limited solubility in alcohol, and insoluble in ether. Found: C 11.21; F 16.56; S 14.56%. C₂O₅F₂SN₂. Calculated: C 10.91; F 17.20; S 14.57%.

TABLE 2

Formula	NaOH		F ⁺		Cl	
	found	calcu- lated	found	calcu- lated	found	calcu- lated
F—SO ₂ —CF ₂ —CO—OH	3,01	3,00	1,02	1,00	—	—
(F—SO ₂ —CF ₂ —CO—) ₂ O	5,95	6,00	2,05	2,00	—	—
F—SO ₂ —CF ₂ —CO—Cl	3,95	4,00	1,02	1,00	0,97	1,00
F—SO ₂ —CF ₂ —CO—OC ₃ H ₇ -i	3,05	3,00	0,98	1,00	—	—

Difluoro(fluorosulfonyl)acetic Acid. A polytetrafluoroethylene reactor was charged with 18.0 g of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone, which was stirred and cooled with ice while dropwise addition was made of 1.8 g of water at such a rate that the reaction temperature did not rise above 5°. When the addition of water was complete, the reaction mixture was heated at 100° until hydrogen fluoride was completely removed. The residue (17.7 g of a colorless liquid) was almost pure difluoro(fluorosulfonyl)acetic acid. To obtain a chemically pure product, this preparation was distilled at reduced or atmospheric pressure. Yield 17.1 g (96%). Found: C 13.86; H 0.91; F 31.63; S 18.27%; mol. wt. 175.6. C₂H₂O₄F₃S. Calculated: C 13.48; H 0.55; F 32.00; S 17.97%; mol. wt. 178.1.

Difluoro(fluorosulfonyl)acetic acid is a colorless mobile liquid which fumes slightly in air; it is readily soluble in water and in organic solvent.

Difluoro(fluorosulfonyl)acetic Anhydride. A mixture of 17.8 g of difluoro(fluorosulfonyl)acetic acid and 10.6 g (50% excess) of phosphorus pentoxide was heated in a water bath for 30 minutes. By fractionation of the semiliquid mixture we isolated 16.0 g (95%) of difluoro(fluorosulfonyl)acetic anhydride. Found: C 14.00; F 34.48; S 19.26%; mol. wt. 331.5. C₄O₇F₆S₂. Calculated: C 14.18; F 33.73; S 18.93%; mol. wt. 338.2.

Difluoro(fluorosulfonyl)acetyl Chloride. A mixture of 17.8 g of difluoro(fluorosulfonyl)acetic acid and 23.0 g (10% excess) of phosphorus pentachloride was heated in a water bath until a homogeneous solution was formed (about 30 minutes). By fractionation we isolated 19.3 g (98%) of difluoro(fluorosulfonyl)acetyl chloride. Found: C 12.34; F 28.30; Cl 18.30; S 16.71%; mol. wt. 192.1. C₂O₃F₃ClS. Calculated: C 12.27; F 28.79; Cl 18.05; S 16.53%; mol. wt. 196.6.

Methyl Difluoro(fluorosulfonyl)acetate. Methanol (3.2 g) was added dropwise to 19.7 g of difluoro(fluorosulfonyl)acetyl chloride. By fractionation we isolated 18.9 g (99%) of methyl difluoro(fluorosulfonyl)acetate. Found: C 18.74; H 1.45; F 29.97; S 16.80%; mol. wt. 192.0. C₃H₃O₄F₃S. Calculated: C 18.75; H 1.57; F 29.68; S 16.67%; mol. wt. 192.4.

Ethyl Difluoro(fluorosulfonyl)acetate. This was prepared similarly in 98% yield. Found: C 23.19; H 2.34; F 26.73; S 15.64%; mol. wt. 204.5. C₄H₅O₄F₃S. Calculated: C 23.60; H 2.43; F 27.61; S 15.53%; mol. wt. 206.4.

Isopropyl Difluoro(fluorosulfonyl)acetate. This was prepared similarly in 95% yield. Found: F 25.41; S 14.41%; mol. wt. 221.0. C₅H₇O₄F₃S. Calculated: F 26.00; S 14.54%; mol. wt. 220.0.

Hydrolysis of Difluoro(fluorosulfonyl)acetic Acid and its Derivatives. A weighed sample of the substance was treated with excess of 0.1 N aqueous NaOH. The excess of alkali was back-titrated to phenolphthalein with 0.1 N HCl. Halide ions were determined in the solution (fluoride, thoriometrically; chloride, argentometrically). Table 2 gives the found and calculated equivalents of acid and hydrolyzable halogen.

SUMMARY

1. The hydrolysis of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone was studied.
2. By the controlled hydrolysis of tetrafluoro-2-hydroxyethanesulfonic acid β -sultone, difluoro(fluorosulfonyl)acetic acid was obtained.
3. Various derivatives of difluoro(fluorosulfonyl)acetic acid were prepared.

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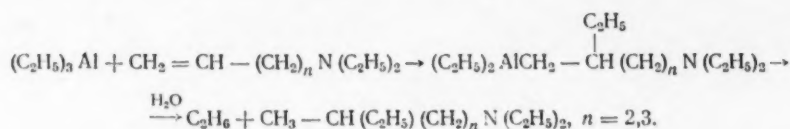
PREPARATION AND PROPERTIES OF SOME
INTERNAL-COMPLEX ORGANOALUMINUM COMPOUNDS

L. I. Zakharkin and L. A. Savina

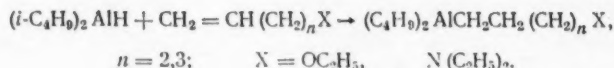
Institute of Heteroorganic Compounds, Academy of Sciences of the USSR
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
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It was shown previously [1] that, under the action of allyl compounds of the type $\text{CH}_2=\text{CH}-\text{CH}_2\text{X}$ ($\text{X} = \text{OR}, \text{NR}_2$, and SR), triethylaluminum does not add at the double bond, as it does in the case of α -olefins [2], but brings about cleavage of the allyl C-X bond with formation of $(\text{C}_2\text{H}_5)_2\text{AlX}$ and 1-pentene. On the other hand, diisobutylaluminum hydride adds smoothly at the double bond of these allyl derivatives with formation of mixed organoaluminum compounds $(i\text{-C}_4\text{H}_9)_2\text{AlCH}_2\text{CH}_2\text{CH}_2\text{X}$.

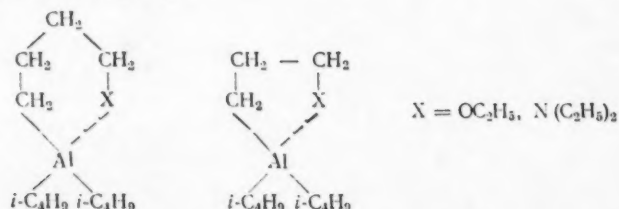
In the present investigation we studied the action of triethylaluminum and of diisobutylaluminum hydride on unsaturated compounds of the type $\text{CH}_2 = \text{CH}(\text{CH}_2)_n\text{X}$, in which $\text{X} = \text{OC}_2\text{H}_5$ and $\text{N}(\text{C}_2\text{H}_5)_2$, and $n = 2$ and 3 . In contrast to its behavior toward allyl derivatives, triethylaluminum adds at the double bonds of *N,N*-diethyl-3-butenylamine and *N,N*-diethyl-4-pentenylamine in accordance with the scheme:



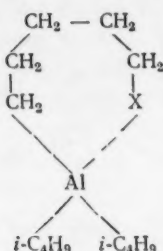
On decomposition of the reaction products with water we isolated *N,N*-diethylhexylamine and *N,N*-diethylheptylamine, respectively. Diisobutylaluminum hydride readily adds at the double bond of the compounds studied in accordance with the scheme:



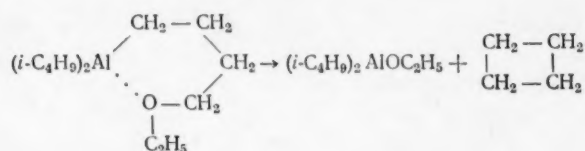
The compounds obtained by the addition of triethylaluminum and of diisobutylaluminum hydride to butenyl derivatives, like the previously described compounds $(i\text{-C}_4\text{H}_9)_2\text{AlCH}_2\text{CH}_2\text{CH}_2\text{X}$, are six- and five-membered cyclic internal-complex compounds of structure



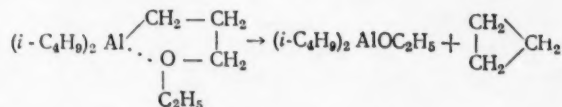
This is confirmed by determinations of molecular weights, which for these compounds correspond to the values calculated from the empirical formulas. Compounds obtained from pentenyl derivatives $[(i-C_4H_9)_2Al(CH_2)_5X]$, in which $X = OC_2H_5$ and $N(C_2H_5)_2$, and $(C_2H_5)_2N(CH_2)_3CH(C_2H_5)CH_2Al(CH_2)_5$ are considerably associated because of the formation of complex bonds between the molecules, for the measured values of the molecular weights are higher than those calculated from the formulas. In consistency these compounds differ greatly from those prepared from allyl and butenyl derivatives: whereas the first are fairly mobile liquids, the latter are extremely viscous. This difference is probably associated with the fact that with $(i-C_4H_9)_2Al(CH_2)_5X$ internal-complex formation must lead to a seven-membered cycle, whose formation must be less favored than that of five- and six-membered cycles, which occurs in the case of propyl and butyl derivatives. From the values of the molecular weights of $(i-C_4H_9)_2Al(CH_2)_5OC_2H_5$ and $(i-C_4H_9)_2Al(CH_2)_5N(C_2H_5)_2$ it follows that not only associated molecules, but also internal-complex seven-membered cyclic molecules are present:



The organoaluminum compounds obtained in the present investigation, and also the previously described $(i-C_4H_9)_2Al(CH_2)_3X$, have considerable thermal stability. Thus, (ethoxybutyl)diisobutylaluminum begins to decompose appreciably with formation of gaseous products only at 230-235°, (ethoxypropyl)diisobutylaluminum at 185-190°, and (ethoxypentyl)diisobutylaluminum at 230°. The thermal decomposition of these compounds does not lead to the formation of the corresponding hydrides, whose formation might be expected on analogy with the thermal decomposition of triisobutylaluminum [3]. Thus, at 230-235° (ethoxybutyl)diisobutylaluminum decomposes with the formation of cyclobutane and ethoxydiisobutylaluminum:



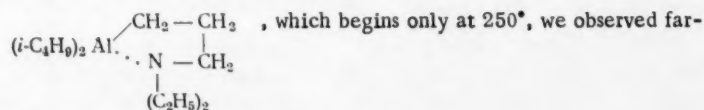
In the case of (ethoxypropyl)diisobutylaluminum, at 185-190° there occurs the elimination of a molecule of cyclopropane and the formation of ethoxydiisobutylaluminum:



In the decomposition the elimination of isobutane is also observed, but no compound containing an Al-H bond was detected.

Cyclobutane, cyclopropane, and isobutene were identified as products of the thermal decomposition of internal-complex organoaluminum compounds with the aid of the infrared spectra.

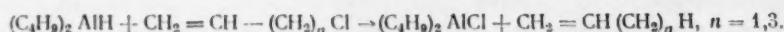
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reaching decomposition of the molecule with liberation of metallic aluminum.

In the present investigation we studied also the action of diisobutylaluminum hydride on allyl chloride and 4-pentenyl chloride with the object of obtaining the compounds $(C_4H_9)_2Al(CH_2)_3Cl$ and $(C_4H_9)Al(CH_2)_5Cl$. However,

in neither case did the hydride add at the double bond, but the chloro compounds were reduced to propene and 1-pentene respectively:



EXPERIMENTAL

We prepared N,N-diethyl-4-pentenylamine by Kharasch's method [4] by the reaction of allylmagnesium chloride with 2-chloro-N,N-diethylethylamine. N,N-Diethyl-3-butenylamine was prepared analogously by reaction between $(C_2H_5)_2NCH_2OC_4H_9$ and $ClMgCH_2CH = CH_2$ [5]. 3-Butenyl ethyl ether was prepared by reaction of allylmagnesium bromide with chloromethyl ethyl ether [6]. The described method was modified by changing the order of addition of reactants, and this resulted in an increase in yield. Allyl bromide (6 g) was added to 12 g of magnesium, and to the resulting Grignard reagent and excess of magnesium we gradually added a solution of 54 g of allyl bromide and 40 g of chloromethyl ethyl ether in diethyl ether with application of cooling. The yield of 3-butenyl ethyl ether was 75-80%. Ethyl 4-pentenyl ether was prepared by the action of alcoholic sodium ethoxide on 4-pentenyl bromide in 50% yield. Ethyl 4-pentenyl ether had: b.p. 117-118°; d_4^{20} 0.7907; n_D^{20} 1.4082; Found: MR 35.63; Calculated: MR 35.70. Found: C 73.57; 73.44; H 12.58; 12.57%. $C_7H_{14}O$. Calculated: C 73.63; H 12.35%.

Triethylaluminum and N,N-Diethyl-4-pentenylamine. With stirring and cooling, 25.8 g of N,N-diethyl-4-pentenylamine was added to 42 g of triethylaluminum. The mixture was heated for eight hours at 135-145°. Vacuum distillation gave 29 g of diethyl(diethylaminoheptyl)aluminum,* b.p. 120-122° (1 mm), a very viscous clear liquid. Found: C 70.86; 70.73; H 13.55; 13.41; Al 10.59; 10.85%. $C_{15}H_{34}Al$. Calculated: C 70.54; H 13.42; Al 10.56%.

With efficient cooling, 26.5 g of the substance was decomposed in ether solution with water. The precipitate was dissolved by addition of alkali. The aqueous layer was extracted with ether, and the ether solution was dried with magnesium sulfate. Vacuum distillation gave 13.5 g of N,N-diethylheptylamine; b.p. 95-96° (25 mm); n_D^{20} 1.4320; d_4^{20} 0.7817; Found: MR 56.72; Calculated: MR 56.94. Found: C 77.02; 77.12; H 14.72; 14.50; N 8.30; 8.37%. $C_{11}H_{25}N$. Calculated: C 77.11; H 14.70; N 8.19%.

Triethylaluminum and N,N-Diethyl-3-butenylamine. With cooling and stirring, 11 g of N,N-diethyl-3-butenylamine was added dropwise to 24.5 g of triethylaluminum. The mixture was heated for nine hours at 140-145°. It was then decomposed with water under efficient cooling. We isolated 4.7 g of N,N-diethylhexylamine; b.p. 78° (25 mm); n_D^{20} 1.4248; d_4^{20} 0.7702; Found: MR 52.20; Calculated: MR 52.32; Found: C 76.21; 76.22; H 14.50; 14.33; N 9.05; 9.15%. $C_{10}H_{23}N$. Calculated: C 76.35; H 14.73; N 8.92%.

N,N-Diethyl-4-pentenylamine and Diisobutylaluminum Hydride. The hydride (14 g) was added with stirring to 28 g of N,N-diethyl-4-pentenylamine. The reaction mixture was heated at 80-85° for seven hours. The excess of amine was distilled off under reduced pressure. Vacuum distillation gave 22.3 g of (5-diethylaminopentyl)diisobutylaluminum, b.p. 170-172° (1 mm), a very viscous clear liquid. Found: C 72.10; 72.37; H 13.51; 13.35; Al 9.48; 9.66%. $C_{17}H_{38}AlN$. Calculated: C 72.03; H 13.50; Al 9.51%. The molecular weight, determined cryoscopically in benzene, was 439.0; the calculated value was 285.4.

Ethyl-4-Pentenyl Ether and Diisobutylaluminum Hydride. Diisobutylaluminum hydride (14.5 g) was added with stirring to 28 g of ethyl 4-pentenyl ether. The reaction mixture was heated for seven hours at 75-80°. Excess of the ether was distilled off under reduced pressure. Vacuum distillation gave 20.5 g of (5-ethoxypentyl)diisobutylaluminum, b.p. 122-123° (1 mm). Found: C 69.92; 69.99; H 12.84; 12.83; Al 10.77; 10.96%. $C_{15}H_{33}AlO$. Calculated: C 70.25; H 12.97; Al 10.51%. Values of molecular weight, determined cryoscopically in benzene, were 418.7 and 414.09; the calculated value was 256.3.

N,N-Diethyl-3-butenylamine and Diisobutylaluminum Hydride. A mixture of 14 g of diisobutylaluminum hydride and 27 g of N,N-diethyl-3-butenylamine was heated for six hours at 85-90°. Vacuum distillation gave 23.2 g of (4-diethylaminobutyl)diisobutylaluminum, b.p. 104-105° (1 mm). Found: C 71.27; 71.49; H 13.48; 13.53; Al 10.21; 10.32%. $C_{17}H_{36}AlN$. Calculated: C 71.32; H 13.47; Al 10.02%. The molecular weight, determined cryoscopically in benzene, was 267.9; the calculated value was 269.4.

*Here and elsewhere in this paper "hexyl" and "heptyl" are used loosely (as in the original) to described branched C_6 and C_7 groups, respectively. The structures of these groups can be seen from the equations given in the introduction. — Publisher.

3-Butenyl Ethyl Ether and Diisobutylaluminum Hydride. A mixture of 21 g of diisobutylaluminum hydride and 47 g of 3-butenyl ethyl ether was heated for five hours at 85-90°. The excess of the ether was distilled off at atmospheric pressure. Vacuum distillation gave 29.1 g of (4-ethoxybutyl)diisobutylaluminum, b.p. 100-101° (1.5 mm). Found: C 68.99; 69.19; H 12.89; 13.07; Al 11.34; 11.42%. $C_{14}H_{31}AlO$. Calculated: C 69.26; H 12.89; Al 11.13%. The molecular weight, determined cryoscopically in benzene, was 251.1; the calculated value was 242.3.

Diisobutylaluminum Hydride and Allyl Chloride. Dropwise addition was made at room temperature of 11 g of allyl chloride to 20 g of the hydride dissolved in hexane. At the end of the addition the liberation of gas became appreciable, heat was evolved, and a reddish-brown deposit appeared on the walls of the flask. The reaction mixture was cooled and kept at 35-40°. On the next day the reaction mixture was heated to 60-70° for five hours. In a trap connected with the condenser we collected 2.5 ml of propene, from which we obtained the dibromide; b.p. 141°; n_D^{20} 1.5200. For 1,2-dibromopropane the literature [7] gives: b.p. 140.7-140.8° (740 mm); n_D^{20} 1.5206.

Fractionation of the reaction mixture gave diisobutylaluminum chloride, b.p. 108° (1 mm). Found: C 54.09; 54.43; H 10.45; 10.45; Al 15.96; 15.57; Cl 19.83; 19.78%. $C_8H_{18}AlCl$. Calculated: C 54.33; H 10.19; Al 15.27; Cl 20.11%.

4-Pentenyl Chloride and Diisobutylaluminum Hydride. To 10.5 g of 4-pentenyl chloride we added 11 g of diisobutylaluminum hydride, at first at room temperature, and then at 60-70°. From time to time the flask was cooled to keep the temperature constant. The mixture was heated for eight hours at 60-70°. Vacuum distillation gave 11 g of a substance of b.p. 105° (1 mm) and n_D^{20} 1.4510, which was found to be diisobutylaluminum chloride, for which the literature [8] gives: b.p. 108° (1 mm); n_D^{20} 1.4510. In a trap connected to the reaction flask and cooled with solid carbon dioxide we collected 2-2.5 ml of liquid, from which we isolated 1-pentene; b.p. 30-32°; n_D^{20} 1.3729. For 1-pentene the literature [9] gives: b.p. 30.1°; n_D^{20} 1.3716.

Thermal Decomposition of (3-Ethoxypropyl)diisobutylaluminum. When (3-ethoxypropyl)diisobutylaluminum (19 g) was heated, the liberation of gaseous products became appreciable at 185°. The decomposition was carried out 185-190° and was complete in two hours. Further heating at 190-195° for ten hours did not lead to the liberation of any gaseous products. No separation of metallic aluminum was observed. The gas obtained after the decomposition of a test sample from the reaction mixture with water did not contain hydrogen. Fractionation of the reaction mixture (13.5 g) gave 7.1 g of ethoxydiisobutylaluminum; b.p. 122-123° (2 mm); n_D^{19} 1.4300. Found: C 64.03; 64.22; H 12.37; 12.30; Al 14.84; 14.58%. $C_{10}H_{23}AlO$. Calculated: C 64.48; H 12.45; Al 14.50%. The infrared spectrum of the substance that collected in the trap connected with the reaction flask showed that it was cyclopropane.

Thermal Decomposition of (4-Ethoxybutyl)diisobutylaluminum. (4-Ethoxybutyl)diisobutylaluminum (31 g) was heated at 230-235° for six hours. No separation of metallic aluminum was observed. In the trap connected with the reaction flask there collected 10 ml of liquid. The gas obtained after the decomposition of a test sample from the reaction mixture with water did not contain hydrogen. Fractionation of the reaction mixture gave 8.3 g of ethoxydiisobutylaluminum; b.p. 122-123° (2 mm); n_D^{20} 1.4405. Found: C 64.79; 64.57; H 12.17; 12.27; Al 14.60; 14.38%. $C_{10}H_{23}AlO$. Calculated: C 64.48; H 12.45; Al 14.50%. At room temperature, the liquid that collected in the trap was a gas consisting of 82% saturated and 17% unsaturated hydrocarbons. The infrared spectrum showed that the mixture consisted of cyclobutane and isobutane.

The spectra were determined with a double-beam infrared spectrometer designed on the basis of the IKS-11 monochromator by T. A. Sidorov, to whom the authors express their thanks.

SUMMARY

1. A study was made of the addition of triethylaluminum and of diisobutylaluminum hydride to the compounds $CH_2 = CH(CH_2)_nX$ ($n = 2$ and 3 ; $X = OC_2H_5, N(C_2H_5)_2$).
2. Compounds of the type $R_2Al(CH_2)_nX$, ($n = 3$ and 4 ; $X = OC_2H_5, N(C_2H_5)_2$) are internal-complex cyclic compounds and are monomeric. On the other hand, $R_2Al(CH_2)_5X$ are not monomeric, but associated, and, together with internal-complex seven-membered compounds, they contain structures with intermolecular complex bonds.
3. In the thermal decomposition of $(i-C_4H_9)_2Al(CH_2)_nOC_2H_5$ in which $n = 3$ and 4 , cyclopropane and cyclobutane, respectively, are formed.

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*Original Russian pagination. See C. B. translation.

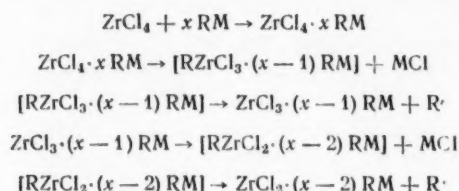
REACTIONS OF ORGANOMETALLIC COMPOUNDS
WITH HEAVY-METAL SALTS

COMMUNICATION 2. REACTION OF ETHYLLITHIUM
WITH COBALT AND TITANIUM HALIDES

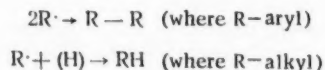
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 6, pp. 1044-1048, June, 1960
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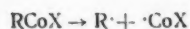
The reactions of organolithium compounds with metal halides have been described mainly in connection with attempts to prepare the corresponding organometallic compounds [1-3]. A series of investigations was carried out by Gilman and co-workers [4]. Gilman divided metal halides into three groups according to the character of the product of reaction with methyllithium: those in the first group (TiCl_4 , ZrCl_4 , TaCl_5 , MnBr_2 , CrCl_3 , LaCl_3) give only methane, those in the second (AgBr , CuCl , CuI , CuCl_2) give only ethane, and those in the third (AuCl_3 , FeCl_2 , NiCl_2) give mixtures of methane and ethane in various proportions. The authors consider that the process goes via intermediate organometallic compounds, whose decomposition leads to free radicals and then to products of their recombination, disproportionation, or hydrogen abstraction, depending on the nature of the radical. In a general form, these reactions are represented by Gilman [5] in a scheme which he gives for the case of a zirconium salt and which is accepted by almost all of the subsequent investigators [6, 7]



(in a similar way, further reduction to metal may occur)

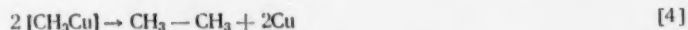


This scheme is very close to that of Kharasch, which he proposed for the reaction of organomagnesium compounds with cobalt chloride [8]; it is again considered that intermediate organocobalt compounds decompose with formation of free radicals:

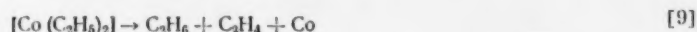


The liberation of gaseous hydrocarbon products observed in these reactions and also the polymerization of some vinyl compounds, even compounds such as ethylene and propene, is attributed by various authors to the action of free radicals [3, 5, 6].

In some papers it has been supposed that reaction may proceed without free-radical stages, e.g., as a result of bimolecular decomposition:



or



However, the authors give no direct experimental proofs in favor of these views.

It is known that the extremely active methyl and ethyl radicals react in hydrocarbon media mainly by abstraction of hydrogen with formation of methane and ethane. The parts played by disproportionation and recombination (for ethyl) are small. Hence, when there is a free-radical stage, it is always to be expected that there will be a predominant amount of saturated hydrocarbons in the reaction products.

It is known also that these free radicals add almost quantitatively to double bonds of the vinyl type. Thus, in the thermal decomposition of methylphenyltriazene in cumene, the reaction proceeds smoothly in the direction of methane formation. In the decomposition of the same triazene in α -methylstyrene the free radicals formed are quantitatively trapped, and methane formation is completely suppressed [10]. In the case of 1-heptene the yield of methane is greatly reduced. The reactivity of free ethyl radicals in addition reactions at double bonds is the same [11].

In view of these considerations, it was considered to be desirable to study the reactions of ethyllithium with cobalt and titanium chlorides in presence of acceptors for free radicals. When free-radical stages are present, reaction cannot lead to the formation of ethane and ethylene. An analogous investigation was carried out for the reaction of organomagnesium compounds with metal halides [12].

We carried out all the reactions in solvents (benzene, *m*-xylene) at 20°. In view of the fact that α -methylstyrene polymerizes under the conditions for reaction under the influence of ethyllithium and titanium tetrachloride, its addition to the reaction mixture was made in portions as the experiment progressed so that a sufficiency of free olefin was always maintained in the mixture. As the experimental results show (Table 1), the presence of free-radical acceptors does not result in the disappearance of ethane and ethylene from the products of the reaction of ethyllithium with cobalt chloride. This does not affect the relative amounts of ethane and ethylene, which, irrespective of the character of the solvent, are liberated in equimolecular amounts.

Ethyllithium reacts vigorously with a suspension of cobalt chloride or a solution of titanium tetrachloride; the liberation of gaseous products is, in the main, finished in 10-15 minutes, and brownish-black precipitates are formed. When ethyllithium reacts with cobalt chloride, the latter is reduced to the metal, which is confirmed by the quantitative formation of hydrogen on decomposition of the precipitate with hydrochloric acid. It should be noted that in presence of α -methylstyrene a reduction in the total yield of gaseous hydrocarbons is observed, which is associated with the consumption of the alkyl lithium in the addition reaction at the double bond.

Ethylene is almost absent from the products of the reaction of ethyllithium with titanium tetrachloride (Table 2). The fact that polymer separates is a direct indication of its formation during the reaction. The polymerizing power of complex catalysts obtained from alkali-metal alkyls and titanium salts is well known. If the reaction is carried out without vigorous stirring, we observe the liberation of larger amounts of ethylene (20-40% of ethylene on the amount of ethyllithium taken for reaction). * The yield of ethane is almost independent of the nature of the solvent. Neither does α -methylstyrene, which is an effective free-radical acceptor, affect the yield of ethane.

From the above considerations it follows that the oxidation-reduction reactions between ethyllithium and cobalt or titanium halides do not include stages in which the intermediate products behave like free radicals.

*This is probably due to deterioration in the polymerization conditions.

TABLE 1

Products of the Reaction of Ethyllithium with Cobalt Chloride at 20°

No.	LiC ₂ H ₅ (molar) CoCl ₂	Reaction medium	Yield (%)			Ethane liberated in decomposition of residual organometallic comp. with alcohol (ml)	Total yield (%)
			ethyl- lene	ethane	butane*		
1	1:2	Benzene	36	37	2	9	84
2	1:2	Cumene	38	39	5	13	95
3	1:2	Benzene	44	42	7	3	96
4	1:2	Cumene	34	34	5	12	86
5	2:1	Benzene	35	34	7	15	91
6	1:1	m-Xylene	46	54	—	3	103
7	1:2	α-Methylstyrene	28	28	6	2	64
8	1:2	α-Methylstyrene	26	25	13	Nil	64
9	4:1	1,5-Hexadiene	24	22	5	47	98
10	4:1	1,5-Hexadiene	26	23	4	46	99

*The table gives the amount (%) of ethyl radicals reacting with formation of butane; the actual amount of gaseous butane is one-half of this.

TABLE 2

Products of the Reaction of Ethyllithium with Titanium Tetrachloride at 20°

No.	Reaction medium	Yield (% on ethyl- lithium)		
		ethane	ethyl- lene	polyethylene isolated
1	m-Xylene	45	0	2,5
2	m-Xylene	50	0	5,0
3	α-Methylstyrene	42	0	Not determined
4	α-Methylstyrene	51	0	« »
5	α-Heptene	53	0	« »
6	Toluene	52	3	« »
7	Toluene	50	3	« »

EXPERIMENTAL

Ethyllithium was prepared by the usual method in dry benzene from lithium and ethyl chloride. The concentration of ethyllithium was determined by the double-titration method or from the amount of ethane liberated in the course of decomposition with water. To replace the solvent, the benzene was removed in a vacuum and the required solvent was added. Anhydrous cobalt chloride was prepared from the hexahydrate, which was first dried at 100° in a vacuum to the dihydrate. This was then dried at 235-245° [13] in a stream of dry hydrogen chloride, treated at the same temperature with a stream of dry nitrogen, and, for complete removal of traces of hydrogen chloride, exposed to a vacuum at 235-245°. Titanium tetrachloride was prepared by distillation of the commercial product through a column with filling of copper turnings.

The experiments were carried out at 20° until the liberation of gas stopped completely. To prevent solvent vapor from reaching the gas buret, a spiral condenser and trap immersed in a cooling bath (from -10° to -15°) in a Dewar vessel was placed between the apparatus and the gas holder. The experiments were carried out in an apparatus fitted with stirrer (Fig. 1). So that the tube carrying nitrogen did not become blocked with cobalt chloride, it was plugged with glass wool. By alternate evacuation and filling with dry nitrogen, air was displaced, and then in a countercurrent of nitrogen a weighed sample of cobalt chloride was introduced; a little solvent was added, and a solution of ethyllithium in benzene was added dropwise from a funnel. In the case of titanium tetrachloride the weighed sample was introduced in a thin-walled ampoule or as a solution. When the components were mixed, gas was liberated and was collected in a gas holder over saturated brine.

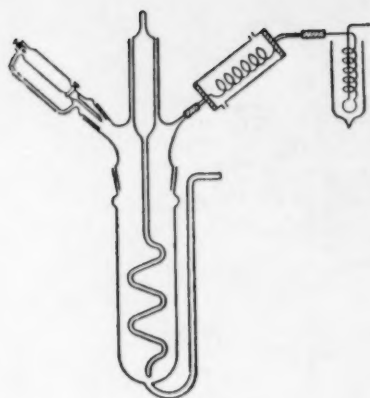


Fig. 1.

When the liberation of gas stopped, the reaction ampoule was heated to 60-80° with passage of nitrogen to remove dissolved gas. The reaction mixture was then decomposed with methanol or saturated sodium chloride solution. The amount of unconsumed ethyllithium was estimated from the amount of ethane then liberated. Both gases were analyzed for hydrogen and unsaturated and saturated hydrocarbons. The unsaturated hydrocarbons were absorbed with bromine water; the saturated hydrocarbons were determined by combustion over cupric oxide, and hydrogen by combustion over palladized asbestos.

Reaction of Ethyllithium with Titanium Tetrachloride. A thin-walled ampoule containing 2.34 g (0.012 mole) of titanium tetrachloride was introduced into a nitrogen-filled 100-ml reaction vessel (Fig. 1). The vessel was placed in a thermostat, and 32 ml of a solution of 1.77 g (0.049 mole) of ethyllithium was introduced. The ampoule was broken by shaking the vessel. A brownish-black flocculent precipitate formed, and gas began to be liberated and was collected in the gas holder over a period of 4-5 hours.

When the liberation of gas stopped, dry nitrogen was bubbled through the system. In all we collected 1855 ml (STP) of gas, in which we found 30.6% (559 ml) of ethane, i.e., 50% of the theoretical amount calculated on the amount of ethyllithium taken for reaction. No unsaturated hydrocarbons were found in the gas. In other experiments small amounts of ethylene were found.

The reaction ampoule was connected with another gas holder, the mixture was decomposed with methanol, the liberated gas was collected, and the apparatus was purged with nitrogen. We collected 2012 ml (STP) of gas, in which we found 10.4% (216 ml) of hydrogen and 9.6% (200 ml) of ethane (18% yield). The whole reaction mixture was then poured into a beaker containing methanol; white flocs of polymer were precipitated. When these were washed we obtained 0.053 g of polyethylene.

The experiment in presence of α -methylstyrene was started similarly to the above with the preliminary addition of 15 ml of α -methylstyrene to the mixture. Then, in the course of the experiment, a further 20 ml of α -methylstyrene was added with stirring. In other respects that procedure was as before.

Reaction of Ethyllithium with Cobalt Chloride. The reaction vessel was filled with nitrogen, and 5.0179 g (0.0386 mole) of cobalt chloride was introduced. The vessel was placed in a thermostat, and 10 ml of dry benzene and 14.7 ml of a 0.81 N benzene solution of ethyllithium (0.695 g, 0.0193 mole) was added from a Schlenk vessel. There was an immediate vigorous evolution of gas, which was collected in a gas holder over a period of 1.5-2 hours. At the end of the reaction the vessel was heated to 60° and purged with dry nitrogen. We collected 1890 ml (STP) of gas, and this contained 42% (178 ml) of ethane, 44% (182 ml) of ethylene, and 7% (14 ml) of butane, i.e., 92% on the amount of ethyllithium taken.

The reaction vessel was connected to another gas holder, and the mixture was decomposed with methanol; the gas liberated was collected. The apparatus was heated to 60° and purged with nitrogen. The gas collected amounted to 470 ml (STP). The yield of ethane was 3% (14 ml).

In the experiments with acceptors, after the introduction of the cobalt chloride, α -methylstyrene or 1,5-hexadiene was added, and then the ethyllithium solution. In other respects the experiments were carried out in the same way as in the case of titanium tetrachloride.

SUMMARY

1. A study was made of the reaction of ethyllithium with titanium tetrachloride and with cobalt chloride at 20° in hydrocarbon solvents and also in presence of unsaturated hydrocarbons as acceptors of free radicals.
2. In the reaction of ethyllithium with cobalt chloride equimolecular amounts of ethane and ethylene are liberated; in the reaction with titanium tetrachloride only ethane is liberated, and ethylene is polymerized. In both of these cases the introduction of acceptors does not effect the composition of the reaction products.
3. The results indicate that the formation of ethane and ethylene is not associated with the occurrence of intermediate free-radical stages.

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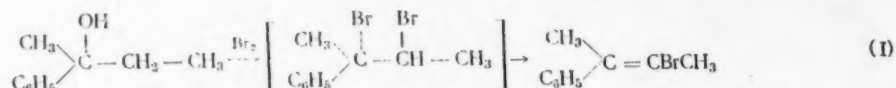
STRUCTURE OF THE BROMO COMPOUND

$C_{10}H_{11}Br$ FORMED BY THE ACTION OF
BROMINE ON 2-PHENYL-2-BUTANOL
OR 2-PHENYL-2-BUTENE

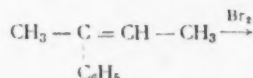
B. M. Mikhailov and I. S. Savel'eva

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Translation from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
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Original article submitted December 1, 1958

By the action of bromine on 2-phenyl-2-butanol [α -ethyl- α -methylbenzyl alcohol] Pansevich-Kolyada and Prilezhaev [1] obtained a bromo compound of composition $C_{10}H_{11}Br$, to which they attributed the structure of 2-bromo-3-phenyl-2-butene (I):



Hell and Bauer [2] attributed the same structure to the bromo compound $C_{10}H_{11}Br$ which they obtained by the action of bromine on 2-phenyl-2-butene:



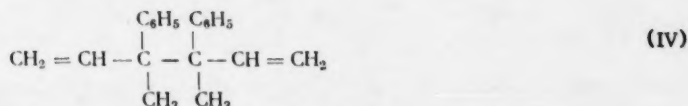
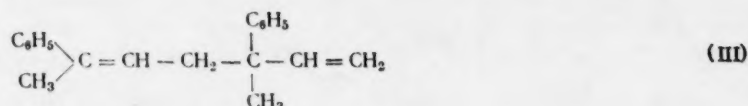
On the basis of the directions given in the literature we undertook the preparation of the bromo compound (I) with a view to its use in further syntheses. Having obtained the bromo compound $C_{10}H_{11}Br$ both by the action of bromine on 2-phenyl-2-butanol and by the action of bromine on 2-phenyl-2-butene, we turned our attention to its lacrimatory properties (which had been noted also by Hell and Bauer and by Pansevich-Kolyada and Prilezhaev), which are not typical of compounds of the vinyl bromide type such as (I).

We doubted the correctness of the structure attributed to the bromo compound $C_{10}H_{11}Br$ by the authors mentioned, and therefore investigated the substance chemically and concluded that it was not 2-bromo-3-phenyl-2-butene (I), but 1-bromo-3-phenyl-2-butene (II):



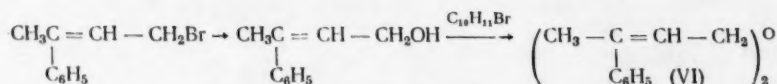
The bromo compound reacted vigorously with magnesium, and only about one-half of the theoretical amount of magnesium was consumed. The reaction gave not an organomagnesium compound, but a mixture of isomeric hydrocarbons of composition $C_{20}H_{22}$, which consisted of the products of the condensation of the organomagnesium compound with the original bromo compound. A similar reaction occurs when cinnamyl chloride is treated with

magnesium, when a mixture of the three possible hydrocarbons of composition $C_{18}H_{18}$ is formed [3]. From our product we isolated a hydrocarbon of m.p. 72-73°, which was either 5-methyl-2,5-diphenyl-2, 6-heptadiene (III) or 3,4-dimethyl-3,4-diphenyl-1,5-hexadiene (IV):

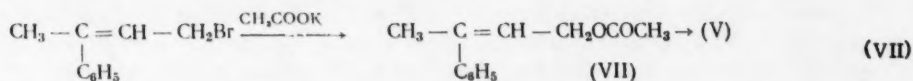


The third possible structure for the hydrocarbon isolated, namely the normal product of the Wurtz reaction 2,7-diphenyl-2,6-octadiene, was excluded because this last hydrocarbon is a liquid [4].

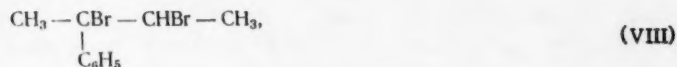
The reaction between the bromo compound under investigation and aqueous potassium carbonate or moist silver oxide took a peculiar course. The product was not 3-phenyl-2-buten-1-ol $\begin{array}{c} \text{CH}_3 - \text{C} = \text{CH} - \text{CH}_2\text{OH} \\ | \\ \text{C}_6\text{H}_5 \end{array}$ (V), but an ether of composition $C_{20}H_{20}O$, which was found to be bis-3-phenyl-2-butenyl ether (VI):



Under the action of potassium acetate the bromo compound was converted into the acetic ester (VII), whose hydrolysis with 1% methanolic hydrogen chloride gave 3-phenyl-2-buten-1-ol (V):

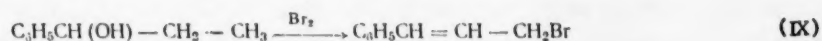


The high mobility of the bromine in the bromo compound investigated indicates that it was undoubtedly of the allyl bromide type and had the structure (II). Hence, on elimination of hydrogen bromide from the dibromo compound (VIII)



which is obtained as an intermediary in the reaction of bromine with 2-phenyl-2-butanol and with 2-phenyl-2-butene, simultaneous rearrangement occurs.

It is clear that data in the literature on the structures of other monobromo compounds formed by the action of bromine on tertiary alcohols [1] and olefins [2] containing aromatic groups will have to be re-examined. Not only tertiary aliphatic-aromatic alcohols, but also secondary aliphatic-aromatic alcohols, are converted into compounds of the allyl bromide type by the action of bromine. Thus, by the action of bromine on α -ethylbenzyl alcohol we obtained a 48% yield of cinnamyl bromide (IX):



This method of obtaining cinnamyl bromide is of preparative significance.

EXPERIMENTAL

1-Bromo-3-Phenyl-2-Butene (II)

a) Preparation from 2-Phenyl-2-Butanol [1]. From 30 g (0.2 mole) of 2-phenyl-2-butanol [5] in 5 ml of carbon tetrachloride and 30.3 g (0.19 mole) of bromine we obtained 18.6 g (44%) of 1-bromo-3-phenyl-2-butene, b.p. 122-125° (19.5 mm) and n_D^{20} 1.5812. After redistillation the bromo compound had b.p. 83-85.5° (1.5 mm).

b) Preparation from 2-Phenyl-2-Butene [2]. From a solution of 72.4 g (0.548 mole) of 2-phenyl-2-butene [5] in 50 ml of chloroform and 87.9 g (0.55 mole) of bromine we obtained 56.6 g (48.2%) of the bromo compound, b.p. 83-85.5° (1.5 mm) and n_D^{20} 1.5810. The literature gives: b.p. 114-116° (13 mm) [2]; b.p. 118-120° (11 mm) and n_D^{20} 1.5811 [1].

Reaction of 1-Bromo-3-Phenyl-2-Butene with Magnesium. A solution of 61 g (0.287 mole) of 1-bromo-3-phenyl-2-butene in 20 ml of dry ether was added dropwise to a mixture of 7 g (0.287 g-atom) of magnesium and 25 ml of dry ether. When the spontaneous evolution of heat ceased, the mixture was boiled for two hours and then decomposed with dilute hydrochloric acid. There remained 3.2 g of unchanged magnesium (45.4%). The organic layer was washed with water and dried over sodium sulfate. Solvent was distilled off, and the residue was fractionally distilled. The fraction of b.p. 140-150° (0.5 mm) (18.7 g) was a mixture of isomeric hydrocarbons of composition $C_{20}H_{22}$. Found: C 91.22; 91.51; H 8.45; 8.55%; mol. wt. 253. $C_{20}H_{22}$. Calculated: C 91.55; H 8.45% mol. wt. 263.4.

Refractionation gave a fraction of b.p. 144-150° (0.5 mm), from which a solid hydrocarbon $C_{20}H_{22}$ crystallized on standing; m.p. 72-73°. Found: C 91.93; 91.83; H 8.54; 8.51%. $C_{20}H_{22}$. Calculated: C 91.55; H 8.45%.

Bis-3-Phenyl-2-Butenyl Ether (VI)

a) A mixture of 19.3 g (0.091 mole) of 1-bromo-3-phenyl-2-butene and 90 ml of 10% aqueous potassium carbonate was boiled for 15 hours. The upper layer was separated, dried with potassium carbonate, and distilled. We obtained 3.33 g of bis-3-phenyl-2-butenyl ether, b.p. 174-176° (3 mm). Found: C 86.32; 86.18; H 8.02; 8.10%. $C_{20}H_{22}O$. Calculated: C 86.29; H 7.97%.

b) 1-Bromo-3-phenyl-2-butene (21 g, 0.099 mole) was added dropwise to a stirred suspension of silver oxide (prepared from 17 g of silver nitrate) in 200 ml of water, after which the reaction mixture was stirred for four hours. On the next day the aqueous layer was decanted and the precipitate was extracted with 150 ml of ether. Solvent was distilled from the ether layer, and the residue was distilled. We obtained the ether (VI) in 30% yield; b.p. 167-169° (2.5 mm).

3-Phenyl-2-Butenyl Acetate (VII)

A mixture of 50 g (0.235 mole) of 1-bromo-3-phenyl-2-butene, 42 g of fused potassium acetate, and 25 ml of glacial acetic acid was heated with periodic shaking at a gentle boil for three hours. Water (100 ml) was then added to the reaction mixture, and the oil formed was separated, washed with water, dried with sodium sulfate, and distilled. We obtained 21 g of 3-phenyl-2-butenyl acetate, b.p. 87.5-90.5° (2 mm). After redistillation the acetic ester had b.p. 87.5-88° (1 mm), n_D^{20} 1.5265; d_4^{20} 1.0369. Found: C 75.89; 75.73; H 7.55; 7.49%; MR 56.35. $C_{12}H_{14}O_2$. Calculated: C 75.76; H 7.42%; MR 56.82.

3-Phenyl-2-Buten-1-ol (V)

A mixture of 15.8 g (0.03 mole) of 3-phenyl-2-butenyl acetate and 15 ml of methanol containing 1% of hydrogen chloride was boiled for 90 minutes. The alcohol was then distilled off, and the reaction products were fractionated. The fraction of b.p. 88-92.5° (1.5 mm) (7.67 g) was refluxed with 10 ml of 10% aqueous potassium carbonate for 11 hours. The upper layer was extracted with ether, the ether solution was dried with sodium sulfate, solvent was distilled off, and the residue was fractionated. We obtained 2.5 g of 3-phenyl-2-buten-1-ol; b.p. 93.5-95° (1 mm); n_D^{20} 1.5505; d_4^{20} 1.0246; Found: MR 46.1; Calculated: MR 48.84. The literature [6] gives: b.p. 105-107° (5 mm); d_4^{22} 0.9696. Found: C 79.68; H 8.06%; mol. wt. 149.4. $C_{10}H_{12}O$. Calculated: C 81.02; H 8.17%; mol. wt. 148.2. The substance contained traces of halogen, which we could not remove even by prolonged heating with aqueous potassium carbonate.

Cinnamyl Bromide (IX)

α -Ethylbenzyl alcohol [7] (92.6 g, 0.68 mole) was heated to 40-45° and stirred while a solution of 34.7 ml (0.68 mole) of bromine in 40 ml of carbon tetrachloride was added dropwise. The reaction mixture was then washed with 5% sodium carbonate solution and with water; the organic layer was dried with sodium sulfate, solvent was distilled off, and the residue was distilled. We obtained 64.8 g (48%) of cinnamyl bromide; b.p. 127-128° (10 mm); m.p. 33°. The literature gives b.p. 130° (10 mm) and m.p. 30° [8]; m.p. 34° [9].

SUMMARY

1. The bromo compound $C_{10}H_{11}Br$ formed by the action of bromine on 2-phenyl-2-butanol or on 2-phenyl-2-butene is not 2-bromo-3-phenyl-2-butene as assumed by Hell and Bauer and by Pansevich-Kolyada and Prilezhaev, but is 1-bromo-3-phenyl-2-butene.

2. The reaction of bromine with α -ethylbenzyl alcohol gives cinnamyl bromide.

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CHEMISTRY OF NITROPYRROLES

COMMUNICATION 5. • PREPARATION OF SUBSTITUTED DINITROPYRROLES

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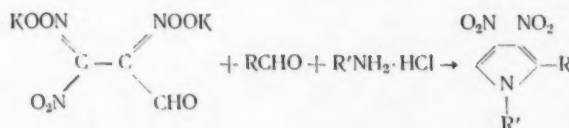
We have previously shown [1] that in the reaction of the dipotassium salt of trinitropropionaldehyde with formaldehyde and methylamine 1-methyl-3,4-dinitropyrrole is obtained. When ethylamine is used in this reaction, the product is 1-ethyl-3,4-dinitropyrrole. With the object of obtaining different substituted nitropyrroles, we studied the behavior of various amines in this reaction, and also replaced formaldehyde by certain other aldehydes. For the reaction we used ammonia, hydrazine, ethylenediamine, urea, aniline, benzylamine, 2-aminoethanol, and glycine ethyl ester. In all cases there was reaction with evolution of heat, feeble liberation of gas, and formation of a solid product. When ammonia, hydrazine, ethylenediamine, and urea were used, we obtained amorphous insoluble precipitates which decomposed under the action of strong acids and from which we did not succeed in isolating any individual substances.

The interaction with aniline was more complex. As a result of the reaction we obtained two substances, which corresponded in elementary analysis to the formulas $C_{16}H_{13}N_3O_2$ and $C_{13}H_{11}N_3O_2$. The structures of these substances were not established.

In the reactions with benzylamine, 2-aminoethanol, and glycine ethyl ester we obtained, respectively, 1-benzyl-3,4-dinitropyrrole (I), 1-(2-hydroxyethyl)-3,4-dinitropyrrole [3,4-dinitropyrrole-1-ethanol] (II), and ethyl 3,4-dinitropyrrole-1-acetate (III).

Hence it is possible to introduce amines containing various functional groups into the reaction with the dipotassium salt of trinitropropionaldehyde and formaldehyde, and this permits the preparation of N-substituted dinitropyrroles. The reaction appears to go in the desired direction with monoacid amines that are strong bases.

Formaldehyde can be replaced in the reaction by its simplest homologs, acetaldehyde and propionaldehyde. The products are then 1,2-dimethyl-3,4-dinitropyrrole (IV) and 2-ethyl-1-methyl-3,4-dinitropyrrole (V). With acrolein, crotonaldehyde, and benzaldehyde, resinous products were obtained.



• For Communication 4 of this series see [2].

The (hydroxyethyl)pyrrole (II) readily exchanges its hydroxyl for bromine under the action of bromine and phosphorus. In presence of a mixture of methanol and concentrated hydrochloric acid, the ethyl pyrroleacetate (III) undergoes transesterification with formation of the methyl ester. Both the methyl and the ethyl esters are readily hydrolyzed under the action of concentrated sulfuric acid with formation of 3,4-dinitropyrrole-1-acetic acid.

EXPERIMENTAL

In all the experiments we started from unpurified dipotassium salt of trinitropropionaldehyde containing about 40% of potassium bromide. For this reason the yields of the 1-substituted 3,4-dinitropyrroles and other compounds obtained were calculated on the basis of 2,3-dibromofumaraldehydic acid.

1-Benzyl-3,4-dinitropyrrole. By the previously described method [1] the dipotassium salt of trinitropropionaldehyde was prepared from 50 g of 2,3-dibromofumaraldehydic acid. The salt was dissolved in water, and a few drops of ammonia solution were added; this was followed by 20 ml of 28% formaldehyde solution and 15 g of benzylamine hydrochloride. The mixture was shaken vigorously and then allowed to stand for 3-4 hours. The reaction started 10-15 minutes after the mixing of the reactants; it went with slight evolution of heat and some liberation of gas, and it was complete in 2-3 hours. The precipitate of fine crystals together with resinous products was separated, washed with water, and dried in the air; it was recrystallized, first from acetic acid, and then from ethanol with the addition of activated charcoal. Yield 8.7 g (18.2%); m.p. 107-108°. After repeated crystallization from ethanol the melting point became 108-109°. Found: C 53.70; 53.87; H 3.70; 3.80; N 16.73; 16.74%. $C_{11}H_7N_3O_4$. Calculated: C 53.44; H 3.65; N 17.00%.

1-(2-Hydroxyethyl)-3,4-dinitropyrrole. Dipotassium salt of trinitropropionaldehyde prepared from 50 g of 2,3-dibromofumaraldehydic acid was dissolved in water and treated with ammonia, formaldehyde, and 2-aminoethanol hydrochloride (11 g) (cf. preparation of 1-benzyl-3,4-dinitropyrrole). After 2-3 hours the precipitated crystals were filtered off, washed with water, dried in air, and crystallized from ethanol. Almost white fine crystals separated when the alcoholic solution was cooled with a mixture of solid carbon dioxide and acetone. The yield was 6.5 g (16.6%); m.p. 77-79°. After further crystallization the melting point did not change. Found: C 36.40; 36.16; H 3.65; 3.60; N 20.82; 20.82%. $C_6H_7N_3O_5$. Calculated: C 35.84; H 3.51; N 20.91%.

1-(2-Bromoethyl)-3,4-dinitropyrrole. A suspension of 1 g of 1-(2-hydroxyethyl)-3,4-dinitropyrrole and 0.3 g of red phosphorus in 10 ml of chloroform was stirred while a solution of 3 g of bromine in 5 ml of chloroform was added. Reaction went with evolution of heat. After the addition of all the bromine the mixture was heated in a water bath with stirring for about one hour; the solid precipitate was filtered off, and the filtrate was evaporated to dryness; the dry residue was crystallized twice from alcohol with the addition of activated charcoal. We obtained 0.32 g (24.5%) of a substance of m.p. 87-87.5°. Found: C 27.34; 27.20; H 2.72; 2.49; N 15.67; 15.52; Br 30.04; 30.05%. $C_6H_6N_3O_4Br$. Calculated: C 27.27; H 2.27; N 15.91; Br 30.30%.

Ethyl 3,4-Dinitropyrrole-1-acetate. Dipotassium salt of trinitropropionaldehyde (prepared from 50 g of 2,3-dibromofumaraldehydic acid) was dissolved in water and treated with a solution of ammonia, formaldehyde, and glycine ethyl ester hydrochloride (15.5 g) (cf. preparation of 1-benzyl-3,4-dinitropyrrole). The reaction started immediately and was complete in 2-3 hours. The product was obtained in the form of a paste. It was warmed with alcohol, and the solution obtained was filtered and cooled. Crystals separated, and were filtered off and recrystallized from alcohol. This gave 4 g of pale-yellow scalelike crystals. A further 2.4 g of the substance was obtained from the mother liquor. Total yield 6.4 g (12%); m.p. 83.5-85°. Found: C 39.66; 39.71; H 4.02; 3.81; N 17.71; 17.55%. $C_8H_9N_3O_6$. Calculated: C 39.47; H 3.73; N 17.28%.

Methyl 3,4-Dinitropyrrole-1-acetate. Ethyl 3,4-dinitropyrrole-1-acetate (0.5 g) was dissolved in methanol (10 ml), 2 ml of concentrated hydrochloric acid was added, and the mixture was left for two days. The crystals that separated in this time were filtered off, washed with water, and dried in a desiccator. We obtained 0.42 g (89%) of the methyl ester, m.p. 113-115°. After recrystallization from ethanol the product had m.p. 114.5-116°. Found: C 36.90; 36.76; H 3.00; 3.03; N 19.05; 18.99%. $C_7H_7N_3O_6$. Calculated: C 36.68; H 3.08; N 18.34%.

3,4-Dinitropyrrole-1-acetic Acid. Ethyl 3,4-dinitropyrrole-1-acetate (9.6 g) was dissolved in 150 ml of concentrated sulfuric acid, and 50 ml of water was added gradually over 10-15 minutes with stirring. The mixture became very hot, and on addition of the last portion of water the acid was precipitated. The mass was poured into an equal volume of water. The mixture was cooled, and the acid was filtered off, washed with water, and dried in air. Yield 7.9 g (93%); m.p. 243-244° (decomp.). After recrystallization from acetic acid the melting point was unchanged. Found: C 33.51; 33.62; H 2.48; 2.38; N 20.75; 20.50%. $C_6H_5N_3O_6$. Calculated: C 33.49; H 2.32; N 19.53%.

Reaction with Aniline. The anil of trinitropropionaldehyde and the aniline salt of this anil were prepared by Torrey and Black's method [3].

I. A mixture of 1 g of the aniline salt of the anil of trinitropropionaldehyde (instead of the salt, the anil and an equivalent amount of aniline can be taken), 15 ml of alcohol, 0.4 ml of 28% formaldehyde solution, and 1-2 drops of aniline was heated until the components dissolved, and to the warm solution 1-2 ml of concentrated ammonia solution was added. The solution became dark red, and when cool there was a precipitate of bright-red needles. The yield was 0.15 g; m.p. 129-130°. After recrystallization from alcohol: m.p. 130-131°. Found: C 68.56; 68.63; H 4.57; 4.76; N 15.15; 15.27%. $C_{16}H_{13}N_3O_2$. Calculated: C 68.82; H 4.66; N 15.05%.

The molecular weight, as determined cryoscopically in benzene, was 288 (duplicate 285); the value calculated for $C_{16}H_{13}N_3O_2$ was 279. Ultraviolet spectrum; $\lambda_{\max} = 285 \text{ m}\mu$ ($\epsilon = 25100$); $430 \text{ m}\mu$ ($\epsilon = 3390$) in alcohol. Frequencies in infrared spectrum (cm^{-1}): 1250, 1340 (NO_2), 1360, 1585, 2930, 2960, 3360 (NH_2 or NH).

II. A mixture of 0.5 g of the anil of trinitropropionaldehyde, 0.174 g of aniline, and 0.2 g of 28% formaldehyde solution was dissolved with slight warming in 15 ml of acetone, and the mixture, which had turned dark in color, was set aside until the acetone had completely evaporated. The dry residue was recrystallized from alcohol or a mixture of dichloroethane and isooctane; the soft fine orange crystals had m.p. 202-203°. The substance was insoluble in alkali and dilute acids; it readily dissolved in concentrated sulfuric acid and could be recovered by pouring the solution into cold water. Found: C 65.37; 65.49; H 4.91; 4.73; N 17.62; 17.67%. $C_{13}H_{11}N_3O_2$. Calculated: C 64.73; H 4.56; N 17.42%.

1,2-Dimethyl-3,4-dinitropropyrole. The dipotassium salt of trinitropropionaldehyde prepared from 25 g of 2,3-dibromofumaraldehydic acid was dissolved in water, and 2-3 drops of ammonia solution, 13 g of methylamine hydrochloride, and 10 ml of acetaldehyde were added. The mixture was warmed slightly and shaken vigorously. Reaction went with feeble liberation of gas; the reaction mixture became dark in color. After 3-4 hours the precipitated crystals were filtered off, washed with water, dried, and crystallized from glacial acetic acid or alcohol. We obtained 0.65 g (3.6%) of substance, m.p. 116-117°. Found: C 38.85; 38.96; H 3.85; 3.82; N 23.70; 23.63%. $C_6H_7N_3O_4$. Calculated: C 38.92; H 3.78; N 22.70%.

2-Ethyl-1-methyl-3,4-dinitropropyrole. This was prepared in a similar way. Yield 2.5 g (13%); m.p. 142-143° (from benzene). Found: N 21.50; 21.60%. $C_7H_9N_3O_4$. Calculated: N 21.11%.

SUMMARY

1. A study was made of the reactions of the dipotassium salt of trinitropropionaldehyde with formaldehyde and a primary amine, those examined being benzylamine, 2-aminoethanol, glycine ethyl ester, aniline, ammonia, hydrazine, ethylenediamine, and urea.
2. The reactions with benzylamine, 2-aminoethanol, and glycine ethyl ester led to the formation of the corresponding nitropropyrole derivatives: 1-benzyl-3,4-dinitropropyrole, 1-(2-hydroxyethyl)-3,4-dinitropropyrole [3,4-dinitropropyrole-1-ethanol], and ethyl 3,4-dinitropropyrole-1-acetate. In the case of ammonia, hydrazine, ethylenediamine, and urea the reaction did not go in the desired direction.
3. In the reaction with aniline two individual substances $C_{16}H_{13}N_3O_2$ and $C_{13}H_{11}N_3O_2$ were obtained; their structures were not determined.
4. It was shown that simple homologs of formaldehyde can be used in the reaction, namely acetaldehyde and propionaldehyde.

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STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 32. syn-cis-3a,4,5,6-TETRAHYDRO-4,5-

INDANDICARBOXYLIC ACID AND ITS STEREOSPECIFIC TRANSFORMATIONS

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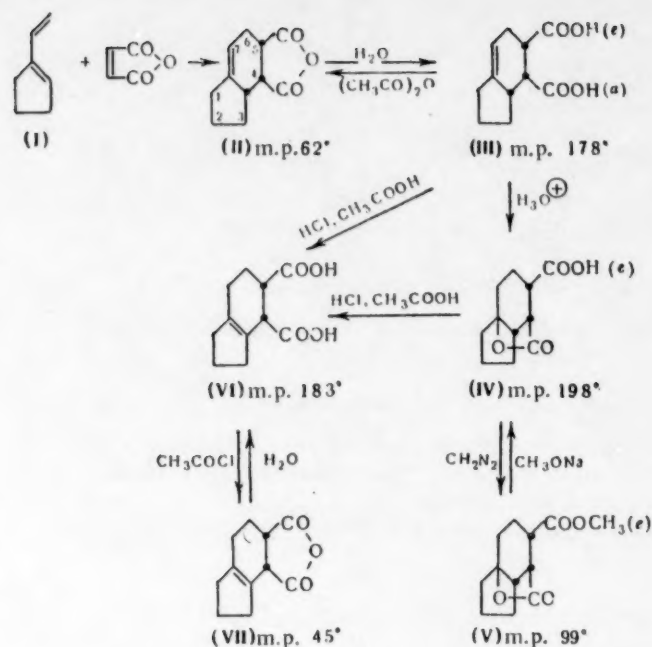
Original article submitted November 28, 1958

As shown previously [1], dicarboxylic acids of the cyclohexene and Δ^4 -octalin series are capable of undergoing separate stereospecific transformations, which may be applied in the proof of their configurations. It was of interest to study the transformations of analogous systems of the tetrahydroindan series, which we may expect to differ from the corresponding Δ^4 -octalin derivatives because of the presence of fusion between five- and six-membered rings.

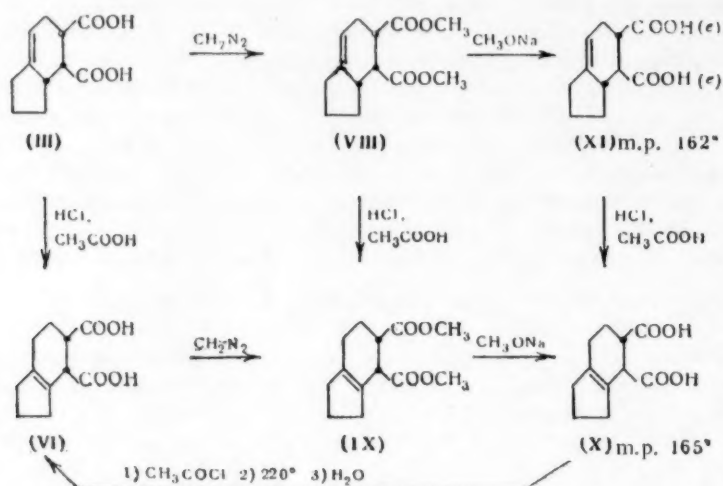
For the synthesis of the required 3a,4,5,6-tetrahydro-4,5-indandicarboxylic acid we made use of the previously described [2] diene condensation of 1-vinylcyclopentene (I) with maleic anhydride. It was found that in this case the reaction, unlike that of 1-vinylcyclohexene [3], proceeds completely stereospecifically and gives only the one adduct (II), which, in accordance with the general laws of the diene synthesis, must have the syn-cis configuration. Hydrolysis of the syn-cis anhydride (II) in a strictly neutral medium gave the corresponding syn-cis-3a,4,5,6-tetrahydro-4,5-indandicarboxylic acid (III). This acid was found to be extremely prone to lactonization, and already in weakly acid aqueous solutions it was readily converted into the corresponding syn-cis γ -lactone acid (IV). We showed that such lactonization can occur even in the hydrolysis of the syn-cis anhydride (II) in presence of a little maleic acid, which is the source of the error made by Dutch investigators [2], who took a somewhat impure sample of the syn-cis γ -lactone acid (IV) to be the syn-cis dicarboxylic acid (III).

The syn-cis γ -lactone ester (V), prepared by treatment of the lactone acid (IV) with diazomethane, has an infrared spectrum characteristic for an ester of a γ -lactone acid ($\nu = 1752$ and 1788 cm^{-1}) [4], and when it was boiled with sodium methoxide it was converted into the original syn-cis γ -lactone acid (IV). This fact shows that the free 5-carboxyl in the γ -lactone acid (IV) has the more stable, equatorial position, and the readiness with which the syn-cis dicarboxylic acid lactonizes with formation of a γ -lactone ring indicates that the 4-carboxyl has an axial position. All these properties confirm the syn-cis configuration for the original adduct (II).

On attempting to obtain the syn-cis γ -lactone acid (IV) by the action of a solution of hydrogen chloride in acetic acid on the syn-cis dicarboxylic acid (III), we obtained a mixture of the expected lactone acid (yield 15-25%) and a new cis-dicarboxylic acid (VI) (yield 25-35%), which we were able to resolve by fractional crystallization. The cis-dicarboxylic acid (VI) is formed in small amounts 3-5% also in the lactonization of the syn-cis dicarboxylic acid (III) in aqueous solution, and when it is treated with acetyl chloride it readily gives the corresponding cis-anhydride (VII), which differs from the original syn-cis adduct (II). It was found that the cis-dicarboxylic acid (VI) is formed in 15-20% yield when a solution of hydrogen chloride in acetic acid reacts with the syn-cis γ -lactone acid (IV). In this respect syn-cis-3a,4,5,6-tetrahydro-4,5-indandicarboxylic acid (III) differs greatly from the previously described 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid [5], and this peculiar feature of its chemical behavior will be examined on the next page.



In order to prove that the cis-dicarboxylic acid (VI) has a double bond between the rings we used the following experimental facts.

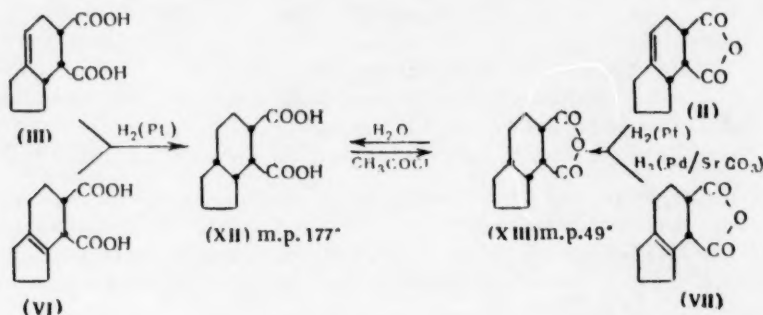


It was found that its cis-diester (IX) is identical with the diester obtained by displacement of the double bond in the original syn-cis diester (VIII). On isomerization with sodium methoxide, the cis-diester (IX) gives the trans-dicarboxylic acid (X), which may be isolated also when the anti-trans dicarboxylic acid (XI), formed by the isomerization of the original syn-cis diester (VIII), is treated with hydrogen chloride in acetic acid. With acetyl chloride the anti-trans dicarboxylic acid (XI) does not give the corresponding anti-trans anhydride, in which respect it differs from the corresponding acid of the Δ^4 -octalin series [6].

From the fact that the trans-dicarboxylic acid (X), after conversion into the anhydride, heating to 215-220°, and hydrolysis, gives the cis-dicarboxylic acid (VI) it follows that these two acids differ only in the configuration

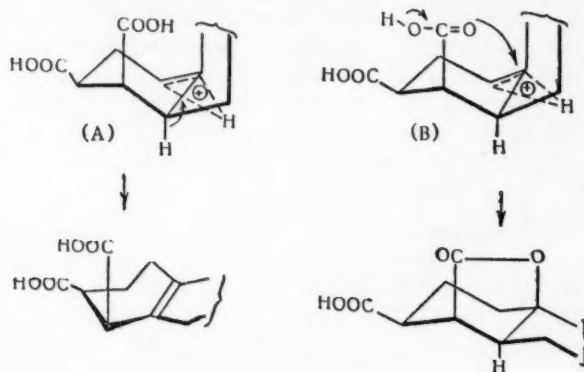
at the carboxyl groups. It is not difficult to see that all these transformations can occur only if the double bond of the cis acid (VI) is situated between the rings, and not in the 3a,4-position. Absorption bands in the 1630-1655 cm^{-1} region, which are characteristic of α,β -unsaturated esters, are absent in the infrared spectrum of the cis-diester (IX), which supports this conclusion.

To prove that the dicarboxylic acids (III) and (VI) are not epimers with respect to C-3a, their catalytic hydrogenation was studied.



It was found that both these acids (III) and (VI) are hydrogenated over a platinum catalyst to the same saturated acid (XII), which, in accordance with the configuration of the original syn-cis acid (III) and the regularities found previously [1] for orientation in hydrogenation, must have the cis-syn-cis configuration. The corresponding anhydrides (II) and (VII) are hydrogenated somewhat less selectively, but here again there is predominant formation of the cis-syn-cis anhydride (XIII), the hydrolysis of which gives the above-described cis-syn-cis-hexahydro-4,5-indandicarboxylic acid (XII).

In order to explain various peculiarities in the chemical behavior of syn-cis-3a,4,5,6-tetrahydro-4,5-indandicarboxylic acid (III) which distinguish it from the corresponding syn-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid, it is necessary to examine its configuration on the basis of conformational concepts with due consideration of the peculiarities resulting from the presence of a five-membered ring. It follows from general views about the mechanism of reactions of unsaturated compounds under the action of acidic agents [7] and from an examination of molecular models that the primary act, both in lactonization and in the displacement of the double bond, is the addition of a proton at the double bond from the least screened side with formation of a π -complex or a nonplanar carbonium ion, which leads to a system with a quasi-cis fusion of rings. Here there arises two possibilities of electron shifts, which determine one or other direction for further reaction.



Shift A, which brings about displacement of the double bond, must in any case lead to increase in the angular strain of the cyclic system. However, the negative steric acceleration [8] will in this case depend only on the absolute value of the difference between the expenditure of energy due to the resulting angular strain and the gain in energy resulting from the change in strain due to the interaction of nonbonded substituents.

When a five-membered ring is present, this difference will probably be less than for the case of a six-membered ring, so that the shift A becomes more probably in the indan system. This view is in good accord with the fact that ΔH for the hydrogenation of 1-methylcyclopentene is lower than that for methylenecyclopentane by 3.8 kcal/mole, whereas in the cyclohexane series this difference is only 2.1 kcal/mole [9]. With regard to formal departures from Braun's principle see [10].

On the other hand, in the nonplanar carbonium ion with a quasi-cis fusion of the rings the shift B, which leads to lactonization, should be favored by the close approach in space of the axial 1,3-substituents. It is known [11] that such steric compacting in the cis-hexahydroindan system is somewhat less than in the cis-decalin system, so that the tendency for the syn-cis dicarboxylic acid (III) to lactonize should be less marked than for its homolog, syn-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid. This factor also makes the shift A, i.e., the displacement of the double bond in the 3a,4,5,6-tetrahydroindan system, more probable. With an equatorial position of the carboxy group shift B is impossible [e.g., in the anti-trans dicarboxylic acid (XI)], and in this case the course of the reaction will be determined only by the probability of the shift A.

The lower stability of the trans-hexahydroindan system as compared with the trans-decalin system [11] can explain the above-noted fact of the opening of the γ -lactone ring in the syn-cis γ -lactone acid (IV) under the action of hydrogen chloride in acetic acid. In accordance with the whole configuration, such a γ -lactone acid has trans fusion of the five- and six-membered rings, which makes it less stable than analogous lactone acids of the trans-decalin series.

EXPERIMENTAL

1-Vinylcyclopentene (I). 1-Ethynylcyclopentanol (110 g of the melt at 25-30°) was hydrogenated over a palladium catalyst (5% Pd). After the absorption of one molecular proportion of hydrogen, the reaction product was vacuum-distilled and gave 105 g (94%) of 1-vinylcyclopentanol, b.p. 68-70° (30 mm) and n_D^{20} 1.4660. When the hydrogenation was carried out in methanol solution, the resulting 1-vinylcyclopentanol formed an azeotropic mixture with the solvent, which rendered isolation difficult and lowered the yield of pure product by 15-20%.

For dehydration, 56 g of 1-vinylcyclopentanol was heated in a stream of nitrogen in a Favorskii flask at 180° with 6.0 g of potassium hydrogen sulfate in presence of 0.1 g of pyrogallol. The diene which then distilled off was separated from the aqueous layer, dried with magnesium sulfate, and again heated under the same conditions with 2.0 g of potassium hydrogen sulfate. After distillation and drying over magnesium sulfate, the diene was distilled over sodium in a feeble stream of nitrogen, and we obtained 23.5 g (48%) of pure 1-vinylcyclopentene (I), b.p. 113-114° and n_D^{20} 1.4860.

Condensation of 1-Vinylcyclopentene with Maleic Anhydride. a) To a solution of 7.0 g of maleic anhydride and 0.1 g of pyrogallol in 30 ml of dry benzene we added 7.50 g of 1-vinylcyclopentene (I). The mixture came to the boil spontaneously (in 10-15 minutes), and it was then heated further for two hours in a water bath, filtered from a little polymer, and vacuum-distilled to remove benzene (bath temperature not above 45°). The crystalline precipitate was filtered off from the oil, washed three times with a 1:3 mixture of diethyl ether and petroleum ether, and dried in a vacuum desiccator. We obtained 12.50 g of the adduct (II), m.p. 56-59°, which after recrystallization from a 3:2 mixture of diethyl ether and petroleum ether had a constant melting point of 61-62° (9.3 g). On partial evaporation of the mother liquor a further 1.15 g of adduct, m.p. 59.5-60.5°, was obtained. The total yield of syn-cis anhydride was 10.45 g (76.5%). Found: C 68.74; 68.48; H 6.46; 6.49%. $C_{11}H_{12}O_3$. Calculated: C 68.72; H 6.30%.

The liquid product remaining after the complete evaporation of the mother liquor was hydrolyzed by boiling it with 10 ml of water (with addition of activated charcoal), and as a result we isolated 0.85 g of the syn-cis dicarboxylic acid (III), decomp. temp. 173-175°. The thick oil remaining after the separation of the crystalline diene-synthesis product was hydrolyzed with 20 ml of boiling water (with addition of activated charcoal), and we obtained 0.70 g of the γ -lactone acid (IV), m.p. 193-195°. The total yield of diene-synthesis products was 86.5% (calculated on syn-cis anhydride).

b) To a solution of 9.0 g of maleic anhydride and 0.1 g of pyrogallol in 50 ml of dry benzene we added at 5° with stirring over a period of 40 minutes 10 g of 1-vinylcyclopentene (I), after which the mixture was stirred further for eight hours at the same temperature and then 16 hours at 15.20°. After the above-described treatment we isolated 10.80 g of the syn-cis anhydride (II) and 1.45 g of the corresponding acid (III).

c) To 5.5 g of maleic anhydride and 0.1 g of pyrogallol, 6.50 g of 1-vinylcyclopentene (I) was added in one portion; in a few minutes the mixture came spontaneously to the boil. The mixture was heated for two hours in a water bath. The resulting viscous reaction product was hydrolyzed by boiling it with 15 ml of water (with addition of activated charcoal). When the solution had cooled, we obtained 7.60 g of heterogeneous crystals, decomp. temp. 150-163°. By fractional crystallization of this mixture from water we succeeded in isolating approximately equal amounts of the syn-cis dicarboxylic acid (III) and the syn-cis γ -lactone acid (IV).

syn-cis-3a,4,5,6-Tetrahydro-4,5-indandicarboxylic Acid (III). A mixture of 12.6 g of twice-recrystallized syn-cis anhydride (II), 10 ml of acetone, and 20 ml of water was boiled until complete dissolution occurred, after which water was added a little at a time and boiling was continued until there was no turbidity when the mixture was cooled. We obtained 12.4 g of the syn-cis dicarboxylic acid (III), decomp. temp. 177-178°, which remained unchanged after recrystallization from acetone. Found: C 62.97; 62.90; H 6.68; 6.73%. $C_{11}H_{14}O_4$. Calculated: C 62.82; H 6.72%.

According to titration with alkali, this acid is dibasic. When the syn-cis dicarboxylic acid (III) was heated with acetic anhydride at 100° for one hour, the original syn-cis anhydride (II) was obtained in good yield.

syn-cis γ -Lactone Acid (IV). a) A mixture of 1.0 g of the syn-cis dicarboxylic acid (III) and 50 mg of maleic anhydride was boiled with 15 ml of water for two hours. Cooling gave 0.87 g of crystals, m.p. 191-193°, and recrystallization gave 0.76 g of the syn-cis γ -lactone acid (IV) with a constant melting point of 197-198°. Found: C 62.90; 62.84; H 6.75; 6.75%. $C_{11}H_{14}O_4$. Calculated: C 62.82; H 6.72%. Values of molecular weight determined by titration with 0.01 N NaOH were 204 and 211.5; the calculated value was 210.

On increase of the amount of maleic anhydride to 0.3 g, we isolated 30 mg of the cis-dicarboxylic acid (VI) from the primary mother liquor.

b) Dry hydrogen chloride was passed for five minutes into a solution of 1.0 g of the syn-cis dicarboxylic acid (III) in 10 ml of dioxane. The crystals that separated were filtered off and washed with three portions of cold water. We obtained 0.55 g of the syn-cis γ -lactone acid (IV), m.p. 197-198°, undepressed by admixture of the above-described specimen. By evaporation of the mother liquor in a vacuum a further 0.40 g of the same lactone acid, m.p. 192-193°, may be isolated.

syn-cis γ -Lactone Ester (V). A solution of 0.30 g of the syn-cis γ -lactone acid (IV) in 5 ml of methanol was treated with an excess of ethereal diazomethane, after which solvent was vacuum-distilled off. We obtained 0.31 g of the syn-cis γ -lactone ester (V), m.p. 94-97°, which had a constant melting point of 98-99° after recrystallization from a 1:3 mixture of diethyl ether and petroleum ether. Found: C 64.30; 64.50; H 7.09; 7.19%. $C_{12}H_{16}O_4$. Calculated: C 64.26; H 7.12%.

The infrared spectrum of the syn-cis γ -lactone ester (V) contains absorption bands characteristic for a five-membered lactone ring and a methoxycarbonyl group ($\nu = 1752$ and 1788 cm^{-1}). On isomerization with sodium methoxide, from 0.25 g of the syn-cis γ -lactone ester (V) we obtained 0.12 g of the original syn-cis γ -lactone acid of m.p. 194-195°.

cis-4,5,6,7-Tetrahydro-4,5-indandicarboxylic Acid (VI). a) A solution of 1.0 g of the syn-cis dicarboxylic acid (III) in 20 ml of glacial acetic acid was saturated with hydrogen chloride and heated at 65° for four hours. Solvent was vacuum-distilled off, and the crystalline residue was washed with three 3-ml portions of ether. We obtained 0.61 g of halogen-free substance, decomp. temp. 158-160°. Crystallization from a large volume of water (35 ml) gave 0.24 g of crystals, decomp. temp. 179-180°, and from the mother liquor, by careful vacuum evaporation to one-quarter bulk, we isolated a further 0.07 g of crystals, decomp. temp. 175-176°, undepressed by admixture of the previous fraction. The two portions of crystals were combined and recrystallized from water. We obtained 0.27 g (27%) of the cis-dicarboxylic acid (VI), decomp. temp. 182-183°; a mixture with the original acid melted at 154-160°. Found: C 62.89; 62.81; H 6.74; 6.72%. $C_{11}H_{14}O_4$. Calculated: C 62.82; H 6.72%.

According to titration with alkali, this acid is dibasic. The main mother liquor was evaporated to one-third bulk, and on standing we isolated 0.22 g (22%) of the syn-cis γ -lactone acid (IV) from it; m.p. 193-195°, undepressed by admixture of the sample obtained previously.

*Under analogous conditions we obtained the corresponding syn-cis γ -lactone acid of the decalin series in 35% yield from syn-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid.

b) A mixture of 1.0 g of the syn-cis γ -lactone acid (IV) and 20 ml of glacial acetic acid was saturated with hydrogen chloride, heated for eight hours at 65°, and then left for three days at room temperature. Solvent was vacuum-distilled off, and 3 ml of ether was added to the viscous residue. The crystalline product formed was filtered off and washed with ether, which gave 0.48 g of halogen-free substance, decomp. temp. 154-160°. By fractional crystallization from water we isolated 0.18 g of substance, decomp. temp. 175-177°, greatly depressed in admixture with the syn-cis dicarboxylic acid (III). Recrystallization from water gave 0.14 g (14%) of pure cis-dicarboxylic acid (VI), decomp. temp. 182-183°, undepressed by admixture of the sample obtained previously.

cis Anhydride (VII). A mixture of 0.50 g of the cis-dicarboxylic acid (VI) and 7 ml of acetyl chloride was boiled for two hours. Volatile substances were vacuum-distilled off, and the liquid residue was dissolved in 10 ml of ether; polymeric impurities were filtered off. Repeated distillation with ether gave 0.29 g of the cis anhydride (VII), which had a constant melting point of 44-45° after crystallization from a mixture of diethyl ether and petroleum ether (with cooling to -40°). Found: C 68.48; 68.80; H 6.49; 6.18%. $C_{11}H_{12}O_3$. Calculated: C 68.72; H 6.30%.

Hydrolysis of the cis anhydride (VII) by boiling it with 30% aqueous acetone gave a quantitative yield of the original cis-dicarboxylic acid, decomp. temp. 182-183°.

syn-cis Diester (VIII). A solution of 4.20 g of the syn-cis diacid (III) in 15 ml of methanol was treated with excess of ethereal diazomethane; solvent was distilled off, and the residue was vacuum-distilled. We obtained 4.1 g of the syn-cis diester (VIII), which, after redistillation, had: b.p. 150-151° (4 mm); n_D^{20} 1.4950; d_4^{20} 1.162. Found: C 65.21; 65.38; H 7.46; 7.40%. $C_{13}H_{18}O_4$. Calculated: C 65.51; H 7.61%.

cis-Diester (IX). a) A solution of 0.85 g of the cis-dicarboxylic acid (VI) in 5 ml of methanol was treated with excess of ethereal diazomethane (distilled). Solvents were distilled off, and vacuum-distillation of the residue gave 0.80 g of the cis-diester (IX); b.p. 151-153° (4 mm); n_D^{20} 1.4720; d_4^{20} 1.153. The infrared spectrum had an intense absorption band at 1742 cm^{-1} , characteristic for the methoxycarbonyl group. Found: C 65.30; 65.78; H 7.43; 7.35%. $C_{13}H_{18}O_4$. Calculated: C 65.51; H 7.61%.

b) A mixture of 1.40 g of doubly distilled syn-cis diester (VIII) and 20 ml of glacial acetic acid was saturated with dry hydrogen chloride and heated at 65° for one hour. Solvent was vacuum-distilled off, and the liquid residue was distilled. Two distillations gave 0.75 g (53.5%) of the cis-diester (IX); b.p. 151-153° (4 mm); n_D^{20} 1.4720.

anti-trans Dicarboxylic Acid (XI). The syn-cis diester (VIII) (3.35 g) was added to a solution of 3.5 g of sodium in 40 ml of absolute methanol, and the mixture was boiled for 18 hours. Methanol was vacuum-distilled off, and the solid residue was dissolved in 40 ml of water; impurities were filtered off, and the solution was boiled with activated charcoal for two hours. The clear solution was evaporated on a steam bath to a thick slurry, and the precipitate of salts was filtered off, washed three times with absolute methanol, and dissolved in 20 ml of water; the solution was warmed and acidified to Congo Red with hydrochloric acid. After one day the precipitated crystals were filtered off, and we obtained 2.10 g of substance, decomp. temp. 158-160°. By evaporation of the mother liquor to half bulk we succeeded in isolating a further 0.25 g of the same substance, decomp. temp. 156-159°. After recrystallization from water we obtained 2.15 g of pure anti-trans dicarboxylic acid (XI), m.p. 161-162° (decomp.); further recrystallization did not raise the melting point. Found: C 63.05; 62.90; H 6.60; 6.67%. $C_{11}H_{14}O_4$. Calculated: C 62.82; H 6.72%.

According to titration with alkali, this acid is dibasic. When an attempt was made to obtain the corresponding anhydride by boiling the acid with acetyl chloride, only the original acid was recovered.

trans-Dicarboxylic Acid (X). a) The cis-diester (IX) (0.5 g) was added to a solution of 1.0 g of sodium in 30 ml of absolute methanol. The mixture was boiled for 15 minutes, methanol was vacuum-distilled off, and the solid residue was dissolved in water; polymeric products were filtered off, and the solution was boiled with activated charcoal for one hour. The clear solution was evaporated on a steam bath to a slurry, and the precipitate of salts was filtered off and washed with absolute methanol. The resulting sodium salt was dissolved in 10 ml of water, and the solution was filtered from polymeric impurities, warmed, and acidified to Congo Red with hydrochloric acid. After one day the precipitated crystals were filtered off, and we obtained 0.37 g of the trans-dicarboxylic acid (X), m.p. 163-164° (decomp.), which, after recrystallization from water, had a constant

decomp. temp. of 164-165°. A mixture test with the anti-trans diacid (XI) showed a definite depression of melting point (147-153°). Found: C 63.05; 63.00; H 6.76; 6.65%. $C_{11}H_{14}O_4$. Calculated: C 62.82; H 6.72%. According to titration with alkali, this acid is dibasic.

b) A solution of 0.35 g of the anti-trans dicarboxylic acid (XI) in 7 ml of glacial acetic acid was saturated with dry hydrogen chloride and heated at 90° for two hours. After one day solvent was vacuum-distilled off, and the colored viscous residue was boiled with 10 ml of water in presence of activated charcoal for one hour. After filtration and cooling of the purified solution we obtained 0.21 g (60%) of the above-described trans-dicarboxylic acid (X), which after repeated crystallization from water had decomp. temp. 164-165° and showed an appreciable depression of melting point in admixture with the original anti-trans dicarboxylic acid (XI) (146-154°).

Thermal Isomerization of the trans-Dicarboxylic Acid (X). The trans-dicarboxylic acid (X) (0.35 g) was boiled with acetyl chloride (5 ml) for 3.5 hours, and volatile products were vacuum-distilled off. The residue* was heated at 215-220° for 40 minutes, after which the liquid reaction product was vacuum-distilled (10 mm) at the same temperature. The resulting clear oil was dissolved in 0.5 ml of acetone, 5 ml of water was added, and the mixture was boiled until dissolution occurred, after which water was added dropwise until the solution ceased to become turbid on cooling. The hot solution was filtered in presence of activated charcoal, and when it was cool 0.16 g of the cis acid (VI) separated, which after recrystallization from water had decomp. temp. 180-181°, undepressed by admixture of a known sample.

cis-syn-cis-Hexahydro-4,5-indandicarboxylic Acid (XII). a) The syn-cis dicarboxylic acid (III) (2.10 g) was hydrogenated as a solution in 30 ml of methanol over 50 mg of platinum oxide. In the course of two hours, one molecular proportion of hydrogen had been absorbed and the catalyst was filtered off; methanol was distilled off, and we obtained 2.05 g of the cis-syn-cis dicarboxylic acid (XII), which after crystallization from water had a constant melting point of 176-177° (decomp.). The yield of pure cis-syn-cis dicarboxylic acid (XII) was above 82%. A mixture test with the original syn-cis dicarboxylic acid (III) showed a great depression of melting point (157-164°). Found: C 62.28; 62.05; H 7.46; 7.48%. $C_{11}H_{16}O_4$. Calculated: C 62.23; H 7.60%. According to titration with alkali, this acid is dibasic.

b) This cis-dicarboxylic acid (VI) (0.21 g) was hydrogenated as a solution in 10 ml of methanol over 50 mg of platinum oxide. The required amount of hydrogen was absorbed in 14 hours. After the above-described treatment we obtained 0.16 g (75.5%) of the cis-syn-cis dicarboxylic acid (XII), decomp. temp. 176-177°, undepressed by admixture of the previous sample.

cis-syn-cis Anhydride (XIII). a) A mixture of 0.60 g of the cis-syn-cis dicarboxylic acid (XII) and 5 ml of acetyl chloride was boiled for two hours, after which volatile products were vacuum-distilled off, the residue was dissolved in 10 ml of ether, and the solution was filtered. Ether was vacuum-distilled off, and this operation of ether distillation was repeated several times until crystallization started. We obtained 0.39 g of substance, m.p. 43-48°. Recrystallization from a mixture of diethyl ether and petroleum ether gave 0.32 g of pure cis-syn-cis anhydride with a constant melting point of 48-49°. Found: C 68.26; 68.19; H 7.12; 7.16%. $C_{11}H_{14}O_3$. Calculated: C 68.01; H 7.27%.

b) The syn-cis anhydride (II) (1.20 g) was hydrogenated as a solution in 10 ml of dry ether over 50 mg of platinum oxide. After the usual treatment we obtained a viscous residue, which did not crystallize at room temperature. Cooling of the hydrogenation product to -40° and treatment with a mixture of diethyl ether and petroleum ether gave 0.75 g of the cis-syn-cis anhydride, m.p. 41-45°, which, after crystallization from a 3:2 mixture of diethyl ether and petroleum ether, had a constant melting point of 48-49°, undepressed by admixture of the above-described sample. From the mother liquors, after hydrolysis with water in presence of activated charcoal, we obtained 0.35 g of the cis-syn-cis dicarboxylic acid (XII), m.p. 176-177°. On hydrogenation of 0.55 g of the cis anhydride (VII) in ether over palladium supported on strontium carbonate [12], we obtained a viscous residue, from which hydrolysis with boiling water gave 0.4 g of the cis-syn-cis dicarboxylic acid (XII), m.p. 176-177°.

SUMMARY

1. A study was made of the condensation of 1-vinylcyclopentene (I) with maleic anhydride and of the stereospecific transformations of syn-cis-3a,4,5,6-tetrahydro-4,5-indandicarboxylic acid (III) which proves its configuration.

*Hydrolysis of the residue with boiling water gave the original trans-dicarboxylic acid (X).

2. The structure and configuration of *cis*-4,5,6,7-tetrahydro-4,5-indandicarboxylic acid (VI), which has an intercycle double bond, were proved, and some of its transformations were described.

3. The catalytic hydrogenation of the isomeric dicarboxylic acids (III) and (VI) and their anhydrides were studied.

4. The mechanism of the lactonization and displacement of the double bond of 3a,4,5,6-tetrahydro-4,5-indandicarboxylic acids was discussed, and their difference in chemical behavior from the corresponding Δ^4 -octalin acids was explained.

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STEREOCHEMISTRY OF ADDITIONS TO A TRIPLE BOND

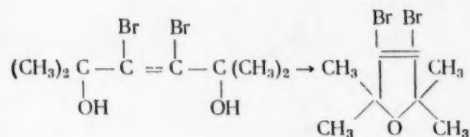
COMMUNICATION 5. STEREOCHEMISTRY OF THE ADDITION OF BROMINE TO DISUBSTITUTED ACETYLENES

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In previous investigations [1, 2] we have studied the stereochemistry of the addition of bromine to mono-substituted acetylenes $RC \equiv CH$ under various conditions. It was shown that the steric orientation in the reaction depends on its mechanism: under conditions of ionic reaction addition is mainly trans, whereas for photochemical bromination in a nonpolar medium cis-dibromo olefins are also formed in an amount which depends on the size of the substituent R. In the present paper we describe the results of a study of the stereochemistry of the addition of bromine to disubstituted acetylenes: diphenylacetylene, 2,5-dimethyl-3-hexyne-2,5-diol, and acetylenedicarboxylic acid.

Under the conditions of photochemical bromination 2-butyne-1,4-diol and 2,5-dimethyl-3-hexyne-2,5-diol form the previously described crystalline dibromo compounds of m.p. 114° [3] and 150° [4], whose configurations have not yet been established. Study of the infrared spectra (absence of a band at 900 cm^{-1}) showed that these bromo compounds are cis isomers. Also, the cis configuration of the dibromide of 2,5-dimethyl-3-hexyne-2,5-diol, m.p. 150°, was confirmed by its dehydration to 3,4-dibromo-2,5-dihydro-2,2,5,5-tetramethylfuran:



The photochemical addition of bromine to 2,5-dimethyl-3-hexyne-2,5-diol is less stereospecific than in the case of 2-butyne-1,4-diol, and it is accompanied by the formation of about 22% of the previously undescribed trans-dibromide, m.p. 129-130°. Still less stereospecific is the photochemical addition of bromine to diphenylacetylene. When the reaction was carried out in hexane we isolated trans- α, α' -dibromostilbene in 69% yield (m.p. 204-206°) and a little of the cis isomer (as a molecular compound with diphenylacetylene, m.p. 76-77°).

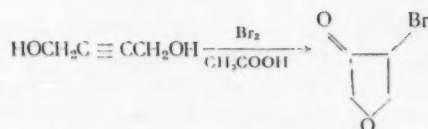
In the study of steric orientation in the ionic reaction, the addition of bromine to 2-butyne-1,4-diol and 2,5-dimethyl-3-hexyne-2,5-diol was investigated in acetic acid in the dark, i.e., under conditions which led mainly to trans-dibromides in the case of propargyl alcohols. It was found, however, that acetylenic diols do not give dibromides under these conditions, because the addition of bromine is suppressed by the participation of the anions of the solvent. Thus, on bromination in acetic acid 2-butyne-1,4-diol gives, as the main reaction

Steric Orientation in the Addition of Bromine to Disubstituted Acetylenes

Acetylenic compound	Bromination conditions	Yield of stereoisomeric dibromides(%)	
		cis	trans
2-Butyne-1,4-diol	In CCl ₄ with irradiation*	84	
	In methanol in the dark	67	
	In N,N-dimethylformamide in the dark	51	
	In N,N-dimethylformamide in the dark in presence of LiBr	48	
2-Butyne-1,4-diol diacetate	In hexane with irradiation*	78	
Acetylenedicarboxylic acid	In ether with irradiation	82	
	In methanol in the dark	12	44
	In N,N-dimethylformamide in the dark		70
2,5-Dimethyl-3-hexyne-2,5-diol	In CCl ₄ with irradiation*	78	16
	In N,N-dimethylformamide in the dark		78
Diphenylacetylene	In hexane with irradiation*		69
	In ether in the dark		81

* Irradiation with a quartz mercury lamp.

product, a substance to which the structure of 4-bromodihydro-3(2H)-furanone must be attributed on the basis of chemical and spectrum data:



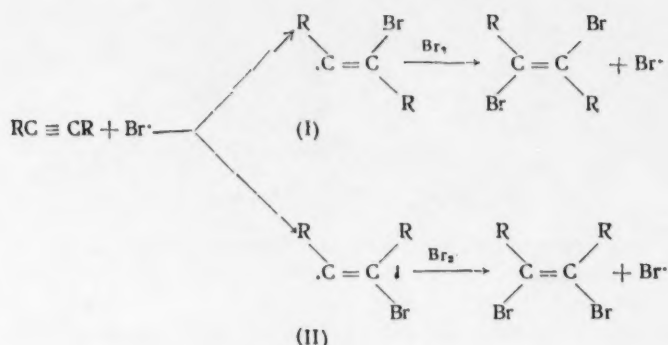
Under these conditions 2,5-dimethyl-3-hexyne-2,5-diol gives a mixture of oily products, which rapidly darken in air with elimination of hydrogen bromide.

Unlike acetylenic diols, acetylenedicarboxylic acid does not react with solvent anions when treated with bromine in an acetic acid medium, but gives a mixture of dibromofumaric and dibromomaleic acids containing not less than 75% of the trans isomer. In presence of two molecular proportions of lithium bromide the reaction becomes stereospecific and leads to pure dibromofumaric acid. We found that dibromofumaric acid and the trans-dibromide of 2,5-dimethyl-3-hexyne-2,5-diol are formed in satisfactory yields in the bromination of acetylenedicarboxylic acid and of 2,5-dimethyl-3-hexyne-2,5-diol in N,N-dimethylformamide. Though more polar than acetic acid, N,N-dimethylformamide does not give anions which interfere in the bromination reaction. In the case of 2,5-dimethyl-3-hexyne-2,5-diol and acetylenedicarboxylic acid the polarity of the solvent is sufficiently high to suppress, apparently completely, homolytic bromination. The reaction becomes stereospecific, and there is scarcely any formation of cis-dibromides.

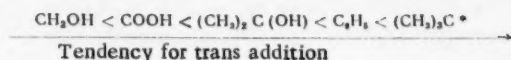
Unlike these acetylenes, 2-butyne-1,4-diol reacts with bromine in N,N-dimethylformamide with formation of cis-dibromide together with a liquid product, which possibly contains the trans form. Addition of large amounts of lithium bromide does not change the steric orientation in the reaction, though in this case the amount of liquid product becomes greater.

On the basis of data on the isomerization of monosubstituted trans-dibromoethylenes to cis-dibromides under the conditions of photochemical reaction [1, 2] it may be assumed that in the case of disubstituted acetylenes the primary products of photochemical reaction are again trans-dibromides. However, our attempts to isomerize trans-2,5-dimethyl-3-hexyne-2,5-diol and dibromofumaric acid in a short irradiation at room temperature in presence of traces of bromine were not successful. Thus, these disubstituted trans-dibromo olefins do not pass into the cis isomers under the conditions of photochemical bromination. This confirms our previous conclusion [2] that cis-dibromides can be formed in the photochemical bromination of acetylenes as a result of "true" cis addition of bromine.

As will be seen from the table, in the disubstituted acetylenes $RC \equiv CR$ the tendency for the formation of cis-dibromides under the conditions of photochemical reaction falls with increase in the size of the substituent R. Such an effect of the substituent on steric orientation in the photochemical reaction may be explained if we assume that this reaction has the character of a chain process:



The stereochemistry of this process is determined in the main by the thermodynamic stabilities of the radicals (I) and (II), which depend in their turn on the relative mutual repulsion of two R substituents ($R \leftrightarrow R$) on the one hand, and that of a bromine atom and an R substituent ($R \leftrightarrow Br$) on the other. When $R \leftrightarrow Br > R \leftrightarrow R$, the radical (II) may be found to be more stable than the radical (I), and the over-all result of the reaction will be cis addition. If, however, the mutual repulsion of two R substituents exceeds the repulsion $R \leftrightarrow Br$ (e.g., when the substituent R is greater in size), trans addition will predominate. In accordance with this the substituents may be arranged in the following series, in which the tendency for the disubstituted acetylene to undergo trans addition of bromine increases



Hence, the size of a substituent has a specific effect on steric orientation in the photochemical addition of bromine to disubstituted acetylenes, and this is in the opposite direction to that observed in series of monosubstituted acetylenes [1, 2].

EXPERIMENTAL

Bromination was carried out under the conditions described in a previous paper [1]. In the case of 2-butyne-1,4-diol and acetylenedicarboxylic acid, whose bromides are readily soluble in water, the reaction mixture was not washed with water and thiosulfate solution, but the solvent and small excess of bromine were driven off in a vacuum at 25-30°. The spectra of 3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diols were determined in chloroform, and the spectrum of 2,3-dibromo-2-butene-1,4-diol was determined in dioxane. As in the case of monosubstituted dibromoethylenes, the spectra of disubstituted trans-dibromides have intense bands at 900 cm^{-1} , which

* Addition of bromine to di-t-butylacetylene in carbon disulfide gives only the trans-dibromide [5].

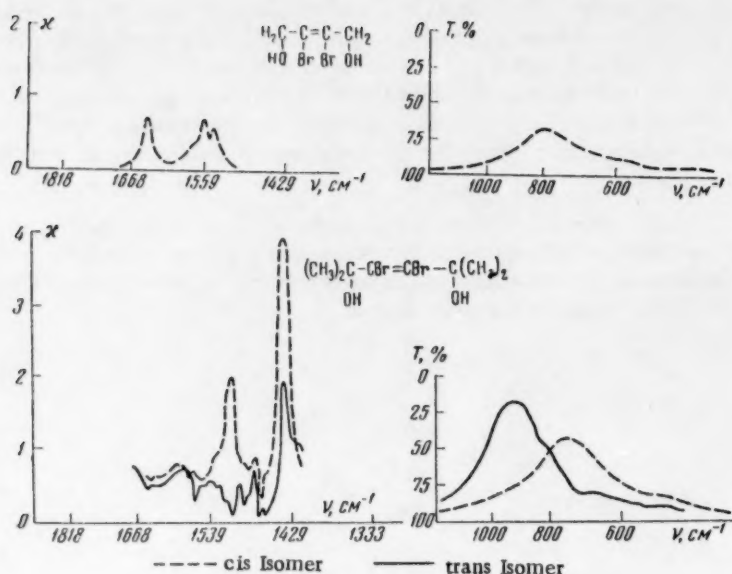


Fig. 1. Infrared spectra of cis-2,3-dibromo-2-butene-1,4-diol and of cis- and trans-3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diols.

are absent in the spectra of the cis isomers. The spectra of the cis-dibromides have an intense absorption band in the region of 1600 cm^{-1} and bands of various intensities at 700 cm^{-1} , which are absent in the spectra of trans-dibromo olefins* (Fig. 1).

Bromination of 2-Butyne-1,4-diol. In carbon tetrachloride. A solution of 19.5 g of bromine in 30 ml of carbon tetrachloride was added dropwise to an irradiated stirred solution of 10 g of 2-butyne-1,4-diol (m.p. 68°) in 900 ml of dry carbon tetrachloride at 55° . When the solution was cooled, crystals were precipitated and were filtered off. Two crystallizations from a 4:1 mixture of benzene and alcohol gave 18.5 g of cis-2,3-dibromo-2-butene-1,4-diol, m.p. $115\text{--}117^\circ$. After distilling solvent from the mother liquor we isolated a further 6.3 g of the cis-dibromobutenediol, m.p. $114.5\text{--}116^\circ$ [3]. The total yield of the cis-dibromobutenediol was 66.8%. After the evaporation of the mother liquors there remained a pale-yellow oil, $n_D^{22} 1.5110$, which probably consisted mainly of 3,4-dibromo-2,5-dihydrofuran. Found: Br 69.68; 69.80%. $\text{C}_4\text{H}_4\text{OBr}_2$. Calculated: Br 70.17%. When left in the air, the oil darkened in color; when vacuum-distilled, it decomposed.

In acetic acid. 2-Butyne-1,4-diol (30 g) was brominated in 95% acetic acid (two hours). Acetic acid and unchanged bromine were distilled off under the vacuum of a water pump at $30\text{--}35^\circ$. The residue consisted of crystals (58 g) and a liquid which rapidly darkened in color. After three crystallizations from a 3:1 mixture of alcohol and hexane we obtained 43 g (70.5%) of a substance of m.p. $59.5\text{--}61^\circ$, to which on the basis of analysis we may attribute the structure of 4-bromodihydro-3(2H)-furanone. Found: C 28.63; 28.67; H 2.92; 2.97; Br 48.70; 48.71%. $\text{C}_4\text{H}_5\text{O}_2\text{Br}$. Calculated: C 29.11; H 3.05; Br 48.44%. Mol. wt. 163 (calculated value 165).

The substance did not give a crystalline 2,4-dinitrophenylhydrazone. Its infrared spectrum contained a characteristic carbonyl absorption band in the region of 1700 cm^{-1} , a very intense band at 1500 cm^{-1} , and an absorption band at 600 cm^{-1} , characteristic for the C—O—C grouping (Fig. 2).

In N,N-dimethylformamide. A solution of 19.5 g of bromine in 30 ml of N,N-dimethylformamide was added dropwise in the dark to a solution of 10 g of 2-butyne-1,4-diol in 30 ml of N,N-dimethylformamide. After two hours, when the solution had almost become decolorized, solvent was distilled off at 1 mm. Water was added, and the precipitated crystals (m.p. $96\text{--}98^\circ$) were recrystallized from ether. We obtained 15.3 g (51%)

*The spectra were determined and interpreted by B. V. Lopatin.

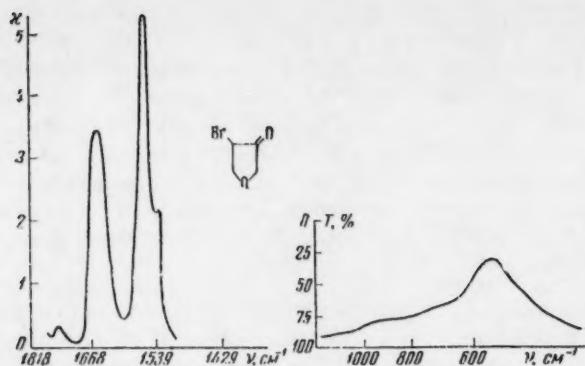


Fig. 2. Infrared spectrum of 4-bromodihydro-3(2H)-furanone.

of *cis*-2,3-dibromo-2-butene-1,4-diol, m.p. 114-116°. On evaporation of the aqueous mother liquor under reduced pressure there remained a sirupy substance which decomposed when distilled. When 10 g of the butynediol was brominated under the same conditions, but in presence of two moles of lithium bromide, 12.9 g of the *cis*-dibromobutenediol was obtained.

Bromination of 2-Butyne-1,4-diol Diacetate. 2-Butyne-1,4-diol diacetate (17 g, 0.1 mole) was brominated under standard conditions [1] with irradiation in 700 ml of hexane. The pale-yellow liquid reaction product (29.2 g) obtained after distilling off the hexane under reduced pressure crystallized on standing. Recrystallization from a 3:1 mixture of benzene and hexane gave 26.1 g (78%) of *cis*-2,3-dibromo-2-butene-1,4-diol diacetate, m.p. 62-63°. Found: C 29.02; 29.18; H 2.93; 2.90; Br 48.36; 48.28%. $C_8H_{10}O_4Br_2$. Calculated: C 29.12; H 3.05; Br 48.44%.

Acetylation of *cis*-2,3-dibromo-2-butene-1,3-diol. Acetic anhydride (24 g) containing *p*-toluenesulfonic acid (0.1 g) was added in portions to 11 g of *cis*-2,3-dibromo-2-butene-1,4-diol. The mixture was heated for one hour at 50° and left overnight at room temperature; 75 ml of water was then added, the mixture was heated for 90 minutes in a water bath, the oil layer was separated, and the aqueous layer was extracted with ether. The combined ether solution was washed with sodium carbonate solution and with water, and was then dried with magnesium sulfate. Ether was distilled off, and crystallization of the residue from a 1:3 mixture of benzene and hexane gave 12.2 g of the diacetate, m.p. 62°. A mixture with the diacetate obtained by the bromination of 2-butyne-1,4-diol diacetate melted without depression.

Bromination of 2,5-Dimethyl-3-hexyne-2,5-diol. In carbon tetrachloride. The dimethylhexynediol (15.7 g) was brominated with irradiation in carbon tetrachloride (600 ml). When the solution was left in a refrigerator, 5.8 g (19%) of crystals of the *trans*-dibromide were precipitated; after recrystallization from ether they melted at 120-130° (see below). After the usual treatment and evaporation of the filtrate under reduced pressure to 100 ml, 22.6 g (78%) of crystals of *cis*-3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diol was precipitated; m.p. 149-150° (from benzene). Found: C 32.11; 32.01; H 4.65; 4.56; Br 53.08; 52.81%. $C_8H_{14}O_2Br_2$. Calculated: C 31.81; H 4.64; Br 52.93%. The mother liquor was evaporated by distillation of the residue under reduced pressure, and a substance of b.p. 84.0-86.6° (10 mm) was obtained; on standing in a refrigerator this yielded crystals. Three crystallizations from alcohol gave 4.8 g of 3,4-dibromo-2,5-dihydro-2,2,5,5-tetramethylfuran, m.p. 49.3-49.5° [4].

In *N,N*-dimethylformamide. A solution of 8 g of bromine in *N,N*-dimethylformamide was added to a solution of 7 g of the dimethylhexynediol in 30 ml of *N,N*-dimethylformamide at 50°. The mixture was kept for 20 hours at 50°, and then diluted with water and extracted with four 100-ml portions of ether. After the usual treatment and drying with magnesium sulfate, the extract was vacuum-evaporated to 150 ml. This led to the precipitation of 11.7 g (78%) of *trans*-3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diol, which melted at 129-130° after two crystallizations from ether. Found: C 32.11; 32.01; H 4.65; 4.56; Br 53.08; 52.81%. $C_8H_{14}O_2Br_2$. Calculated: C 31.81; H 4.64; Br 52.93%. At room temperature the reaction mixture was not completely decolorized in the course of five days.

Bromination of Acetylenedicarboxylic Acid. In methanol. A solution of 8 g of bromine in 40 ml of methanol was added to a stirred solution of 2.8 g of acetylenedicarboxylic acid in 65 ml of methanol. The bromine was added over a period of one hour, during which the temperature of the mixture was kept at 0-5°. The mixture was left for 12 hours at room temperature, and methanol and unchanged bromine were then distilled off at 80 mm. Five crystallizations of the residue from a 5:1 mixture of benzene and ether gave 4.8 g (44%) of dibromofumaric acid, m.p. 231-232° (decomp.). The mother liquors were evaporated, and the liquid residue was distilled at 0.9 mm (bath temperature 130-135°). The liquid distillate (5.95 g) yielded crystals, which were filtered off and recrystallized from a 1:2 mixture of hexane and benzene. Four crystallizations gave 1.2 g of dibromomaleic acid, m.p. 139-140° (in sealed capillary). The liquid part of the distillate (3.75 g) did not crystallize when left for two months.

In ether. A solution of 2.8 g of acetylenedicarboxylic acid and 8 g of bromine in ether was kept in the light for 12 hours at room temperature. The mixture was shaken with dry thiosulfate, ether was distilled off, and the residue was fractionated by crystallization from a 1:2 mixture of hexane and benzene. We obtained 8.9 g (82%) of dibromomaleic acid, m.p. 133-139°, and 0.9 g of dibromofumaric acid, m.p. 228-234°.

Bromination of Diphenylacetylene. In hexane with irradiation. The dibromide obtained after the usual treatment [1] from 9 g of diphenylacetylene was extracted with hot alcohol, in which the trans isomer is poorly soluble [6]. The residue was crystallized from propyl alcohol. We obtained 9.1 g of trans- α,α' -dibromostilbene, m.p. 204-205° [5]. When the alcoholic extract was cooled, a further 1.7 g of the trans isomer was precipitated (total yield 69%). The filtrate was evaporated, and crystallization of the residue from methanol gave 2.7 g of the molecular compound of diphenylacetylene with cis- α,α' -dibromostilbene, m.p. 77° [6].

In ether in the dark. From 9 g of diphenylacetylene we obtained 9.8 g of trans- α,α' -dibromostilbene.

Attempts to Isomerize trans-Dibromides. The experiments were carried out in a quartz vessel. A solution of 1 g of trans-3,4-dibromo-2,5-dimethyl-3-hexene-2,5-diol, m.p. 129-130°, in 100 ml of carbon tetrachloride containing one drop of bromine was irradiated for 30 minutes at 20° with a PRK-4 quartz mercury lamp. The mixture, which had darkened appreciably, was vacuum-evaporated. We recovered 0.82 g of the original trans-dibromide, m.p. 128-129.5°.

A solution of 1 g of dibromofumaric acid in 50 ml of ether was irradiated with a quartz mercury lamp for one hour at 20°. After the solvent was distilled off the original dibromofumaric acid was recovered in almost quantitative yield.

SUMMARY

In the photochemical addition of bromine in nonpolar solvents, 2-butyne-1,4-diol, its diacetate, and 2,5-dimethyl-3-hexyne-2,5-diol form mainly cis-dibromides, whereas diphenylacetylene gives mainly the trans-addition product. Under these conditions the tendency for disubstituted acetylenes to undergo cis addition of bromine falls with increase in the size of the substituent.

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STEREOCHEMISTRY OF ADDITIONS TO A TRIPLE BOND

COMMUNICATION 6. COMPARATIVE STUDY OF STERIC ORIENTATION IN THE ADDITION OF BROMINE TO DISUBSTITUTED ACETYLENES AND OLEFINS

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In continuation of our systematic investigation of the stereochemistry of the addition of bromine to acetylenes [1, 2] we made a comparison of steric orientation in the addition of bromine to disubstituted acetylenes and to their ethylenic analogs under ionic and free-radical conditions. Whereas the *trans* addition of bromine to olefins under the conditions for ionic reaction (in polar solvents without irradiation) may be regarded as fully established [3], the stereochemistry of the photochemical addition of bromine to the double bond has not been studied systematically. In the first place, therefore, we turned our attention to the investigation of the photochemical addition of bromine to olefins. As under the conditions of photochemical bromination many aliphatic olefins are converted into geometric isomers, we chose cyclohexene as our first object for study. In addition, it was found to be possible to study the stereochemistry of the reaction in the case of this *cis* and *trans* forms of 2-butene-1,4-diol, 2-butene-1,4-diol diacetate, and 2,5-dimethyl-3-hexene-2,5-diol (1,1,4,4-tetramethyl-1,2-butene-1,4-diol), which, as preliminary experiments showed, are isomerized only to a slight extent under the conditions of photochemical bromination.

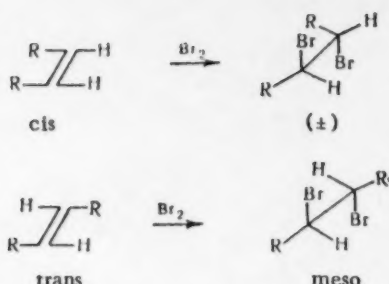
TABLE 1

Relative Rates of Reaction of Diastereoisomeric Dibromides with Potassium Iodide

Original olefin	Constants of dibromide	Amount (%) of dibromide that reacted with KI in methanol at 60° in 40 hours*
<i>cis</i> -2-Butene-1,4-diol	M.p. 86—87°	14
<i>trans</i> -2-Butene-1,4-diol	M.p. 132—134°	22 (1 : 1,5)
<i>cis</i> -2-Butene-1,4-diol diacetate	$n_D^{20} 1,5009^{**}$	8
<i>trans</i> -2-Butene-1,4-diol diacetate		(1 : 2,6)
<i>cis</i> -2,5-Dimethyl-3-hexene-2,5-diol	M.p. 84—86°	21
<i>trans</i> -2,5-Dimethyl-3-hexene-2,5-diol	$n_D^{20} 1,5212^{**}$	3,5
	M.p. 82—83	12 (1 : 3,3)

* The relative amounts of unchanged (\pm)- and meso-dibromides are shown in parenthesis (the amount of unchanged (\pm)-dibromide is taken as unity).

** Not isolated in the pure state.



In all cases the main product of photochemical reaction was the trans-addition product. Thus, in the photochemical bromination of cyclohexene in hexane we obtained a yield of about 90% of trans-1,2-dibromocyclohexane, the configuration of which was confirmed by its constants and Raman spectrum. In the photochemical bromination of stereoisomeric ethylenic diols it was found that one of the two possible diastereoisomeric dibromides was formed predominantly. Its configuration was established by study of its rate of reaction with potassium iodide, for it is known that meso-dibromides react more rapidly with potassium iodide than (±)-isomers [4].

The results of the comparative study of the rates of reaction of potassium iodide with diastereoisomeric dibromides prepared under the conditions for photochemical bromination are given in Table 1.

Table 1 shows that cis-ethylenes were formed in the photochemical bromination of mainly (±)-dibromides, and trans-ethylenes mainly from the meso isomers.

Such steric selectivity in the bromination excludes, in itself, any appreciable isomerization either of the original olefins, or of the (±)- and meso-dibromides under the conditions of the reaction. In the case of the stereoisomeric 2,3-dibromo-1,4-butanediols the absence of isomerization was confirmed by a special experiment.

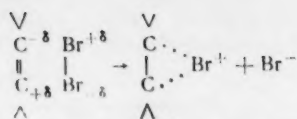
For the stereoisomeric 2-butene-1,4-diol diacetates we showed that steric orientation in the bromination is independent of irradiation or polarity of the solvent. Both under the conditions for photochemical reaction and also in bromination in acetic acid solution in the dark, trans-2-butene-1,4-diol diacetate formed mainly the crystalline meso-dibromide of m.p. 84-86°, and cis-2-butene-1,4-diol diacetate gave the liquid (±)-isomer containing a little of the meso form. As the liquid dibromide obtained by the acetylation of (±)-2,3-dibromo-1,4-butanediol and of known (±)-configuration is partially converted on standing or distillation into the solid isomer, the probable source of the latter in the bromination of the cis-butanediol diacetate is not the cis-addition of bromine, but the isomerization of the (±)-dibromide, the normal trans-addition product.*

It was thus shown that the photochemical bromination of the olefins that we investigated consists in trans addition and does not differ from ionic addition of bromine at a double bond in steric orientation. It was shown also that in this case olefins behave differently from acetylenes of analogous structure, which give mainly cis-dibromides under the conditions of photochemical reaction [2].

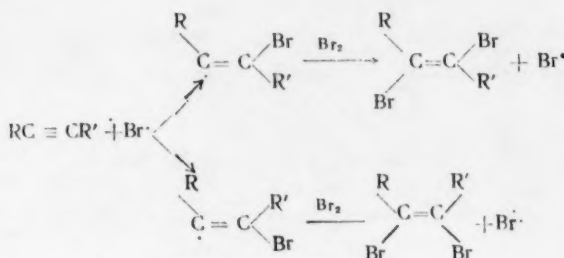
The difference in steric orientation in photochemical bromination between acetylenes and olefins may be due to a difference in mechanism. In the case of acetylenes, bromination in nonpolar solvents is a homolytic reaction, not only under radiation, but also in the dark. The free-radical character of the bromination of 2-butyne-1,4-diol diacetate in toluene is confirmed by the fact that small additions of this acetylenic compound directs the bromination reaction almost entirely in the direction of the formation of benzyl bromide, whereas in absence of the additions a mixture of o- and p-bromotoluenes is the main product. We showed that under the same conditions the bromination of 2-butene-1,4-diol diacetate does not initiate side-chain bromination of toluene. These data show that under given conditions acetylenic compounds may react with bromine by a homolytic mechanism, whereas the bromination of the corresponding ethylenic compounds proceeds by an ionic mechanism.

The cause of this phenomenon must be sought in the different characters of the π-electrons in the ethylenic and acetylenic bonds. Spectrum data indicate that the polarizability of the π-electrons of a double bond is considerably greater than that of the π-electrons of acetylenes [5]. It may be supposed that for this reason olefins in the activated state are able to induce ionization in bromine molecules in a nonpolar solvent. The bromine cations then formed add at a double bond by the usual bromonium mechanism (via a π-complex).

*The lower stability of (±)-2,3-dibromo-1,4-butanediol diacetate, as compared with the free diol (which does not pass into the meso form on irradiation), is to be explained by the relatively great repulsion between a bromine atom and the neighboring acetoxy group even in the most stable conformations of the (±)-isomer.



Acetylenes, which in general have no tendency to form bromonium π -complexes [6], react, on photochemical activation, with bromine atoms by a chain mechanism, the stereochemistry of which is determined mainly by the structure of the acetylenic compound [1, 2].



The structure of the acetylenic compound determines, of course, not only the steric orientation, but also the actual mechanism of bromination. This relation is seen fairly clearly when a comparison is made between the bromination of 2-butyne-1,4-diol and that of 2,5-dimethyl-3-hexyne-2,5-diol in *N,N*-dimethylformamide (Table 2).

The bromination of 2,5-dimethyl-3-hexyne-2,5-diol in *N,N*-dimethylformamide is a heterolytic reaction. This is confirmed not only by the steric orientation of the reaction, but also by the fact that in *N,N*-dimethylformamide the bromination of 2,5-dimethyl-3-hexyne-2,5-diol goes many times more slowly than in carbon tetrachloride, for it is known that the heterolytic bromination of acetylenes is slow in comparison with free-radical reactions [7]. 2-Butyne-1,4-diol is brominated in *N,N*-dimethylformamide at about the same rate as in carbon tetrachloride, and in each case the main product is the *cis*-dibromide.

The formation of the *cis*-dibromide in the bromination of 2-butyne-1,4-diol remains unexplained. As pure *trans*-2,3-dibromo-2-butene-1,4-diol was not available, we could not study its stability. The possibility cannot therefore be excluded that the *cis*-dibromide was formed by the isomerization of the *trans* form. However, the relatively small change in the rate of bromination of 2-butyne-1,4-diol as we pass from a nonpolar to a polar solvent indicates that the reason for the formation of the *cis*-dibromide is the same in each case: reaction in *N,N*-dimethylformamide is to a considerable extent homolytic. In presence of large amounts of lithium bromide the reaction is retarded, possibly because it becomes partly heterolytic. The rate of bromination of 2-butene-1,4-diol in *N,N*-dimethylformamide is comparable with the rate of bromination in carbon tetrachloride and is very little affected by additions of lithium bromide. It is probable that in all three cases the bromination of the ethylenic diol proceeds by the same, heterolytic mechanism.

EXPERIMENTAL

Bromination of Cyclohexene

In Hexane. The bromination was carried out under the radiation of a PRK-4 quartz mercury lamp at 20°. After the usual treatment [1] and fractionation through a column, 16.4 g of cyclohexene gave 41.3 g (92%) of *trans*-1,2-dibromocyclohexane, b.p. 100-102° (13 mm).

In Glacial Acetic Acid in Presence of Lithium Bromide. In the bromination of 16.4 g of cyclohexene in the dark at 20° we obtained 37.3 g (77%) of *trans*-1,2-dibromocyclohexane. Both samples of dibromocyclohexane melted at from -7° to -5°. For *trans*-1,2-dibromocyclohexane the literature [8] gives m.p. -6°; for the *cis* isomer it gives m.p. 9.7-10.5° [9]. The Raman spectra of the two samples were the same.* The frequencies (cm^{-1}) and intensities of the bands at 651 (strong), 685 (weak), and 699 (weak) were in accord with the literature [10].

*The spectra were determined by V. M. Medvedeva.

TABLE 2

Relative Rates of Bromination of Acetylenic and Ethylenic Diols in
0.05 M Solution at 25°*

Original compound	Relative rates of reaction		
	in CCl ₄	in N,N-dimethylformamide	
		in absence of LiBr	in presence of LiBr
trans-2-Butene-1,4-diol	0,8 (trans)	1,3 (trans)	1 (trans)
2-Butyne-1,4-diol	3,5 (cis)	3 (cis)	1 (cis)
2,5-Dimethyl-3-hexyne- 2,5-diol	60 (cis)	1,6 (trans)	1 (trans)

*The predominant direction of the bromination reaction is indicated in parenthesis. The reaction rate in N,N-dimethylformamide in presence of lithium bromide was taken as unity for each diol.

Bromination of cis-2-Butene-1,4-diol

Preliminary experiments showed that in the bromination of the cis-butenediol with an equivalent amount of bromine much hydrogen bromide was liberated toward the end of the reaction, the reaction mixture became dark in color, and the dibromide was obtained in only a low yield. A more satisfactory result was obtained by the use of excess of the butenediol. A solution of 40 g (0.25 mole) of bromine in 40 ml of methylene chloride was added dropwise to an irradiated and stirred mixture of 25.8 g (0.30 mole) of cis-2-butene-1,4-diol, containing not more than 5% of the trans isomer [11], and 100 g of methylene chloride at 0°. Solvent was vacuum-distilled off, and the residue was crystallized from a large volume of benzene. We obtained 44.3 g (72% on the amount of bromine taken) of (±)-2,3-dibromo-1,4-butanediol, m.p. 86-87°. The literature [12] gives m.p. 87°.

Bromination of trans-2-Butene-1,4-diol

The bromination of the trans-butenediol was carried out under the conditions indicated above, but with equivalent amounts of reactants. From 10 g of pure (cis isomer absent [11]) trans-2-butene-1,4-diol we obtained, after crystallization from alcohol, 21.6 g (77%) of meso-2,3-dibromo-1,4-butanediol, m.p. 132-134°. The literature [13] gives m.p. 133-134°. The trans-butenediol brominated appreciably more rapidly than the cis isomer.

Bromination of cis- and trans-2-Butene-1,4-diol Diacetates

In Acetic Acid. Pyridine dibromide hydrobromide [14] (4.2 g) was added in small portions with heating to a solution of 2 g of 2-butene-1,4-diol diacetate (prepared by the acetylation of cis-2-butene-1,4-diol and containing not more than 5% of the trans isomer [11]) in 40 ml of glacial acetic acid. The mixture was left overnight at room temperature; acetic acid was distilled off under the vacuum of a water pump; and ether and water were added to the residue. The ether layer was separated, and the aqueous layer was extracted several times with ether; the combined ether extract was washed with saturated solutions of sodium bicarbonate and sodium thiosulfate and then with water; it was dried with magnesium sulfate. After removal of ether there remained an oil, which partially crystallized out on standing (three days). The crystals (0.5 g), which melted at 84-86° after being washed with ether, showed no depression of melting point in admixture with a sample of meso-2,3-dibromo-1,4-butanediol diacetate prepared by the bromination of trans-2-butene-1,4-diol diacetate (see below).

The oil (5 g, n_D^{20} 1.5012) on distillation [110-112° (0.01 mm)] gave a product which partially crystallized on standing. The crystals melted at 84-86°. The liquid part had n_D^{20} 1.5028; again crystals gradually appeared. Found: C 29.21; 29.11; H 3.64; 3.63; Br 48.48; 48.10%. $C_8H_{12}O_4Br_2$. Calculated: C 28.93; H 3.64; Br 48.14%.

Under the conditions for the bromination of the cis isomer 2 g of pure trans-2-butene-1,4-diol [15] gave 2.6 g (66%) of meso-2,3-dibromo-1,4-butanediol, m.p. 85-86° (from heptane). The literature [13, 16] gives m.p. 86-87°. On bromination with free bromine in acetic acid 3.4 g of the trans-diacetate gave 1.65 g (42%) of the meso-dibromide (yield 42%) and 2.71 g of oil with a low bromine content.

Photochemical Bromination. *trans*-2-Butene-1,4-diol (3.45 g) was brominated in 25 ml of carbon tetrachloride at 20° under the standard conditions for the photochemical reaction [1]. After the usual treatment and removal of solvent by distillation we obtained 4.9 g (76%) of the meso-dibromide, m.p. 85-86° (from heptane). Under the same conditions 3.45 g of the *cis*-butenediol diacetate gave 5.6 g of oil (n_D^{20} 1.5008), from which on standing 0.93 g of crystals of the meso-dibromide, m.p. 84-86°, separated.

Acetylation of (\pm)-2,3-Dibromo-1,4-butanediol

In small portions, 2.32 g of acetic anhydride was added to a mixture of 2.2 g of (\pm)-2,3-dibromo-1,4-butanediol and 0.02 g of *p*-toluenesulfonic acid; the mixture was then left overnight at room temperature. On the next day it was heated for one hour at 50°, 15 ml of water was added, and the mixture was heated for 30 minutes in a water bath. The oil layer was separated from the aqueous solution, which was extracted with ether. The ether extracts were combined with the oil, and the whole was washed with saturated sodium carbonate solution and then with water and was dried with magnesium sulfate. Solvent was distilled off, and there remained 2.57 g of oil, from which a little meso-dibromide was precipitated on standing (m.p. 84-86°). The oil had n_D^{20} 1.5009. Found: C 29.15; 29.02; H 3.60; 3.66; Br 48.29; 48.46%. $C_8H_{12}O_4Br_2$. Calculated: C 28.93; H 3.64; Br 48.14%.

Vacuum distillation of 2 g of the oil at 115-120° (0.02 mm) gave a semicrystalline distillate, from which we isolated 0.6 g of crystalline dibromide, m.p. 85-86°.

Bromination of *trans*-2,5-Dimethyl-3-hexene-2,5-diol

A solution of 3.3 g of bromine in 15 ml of methylene chloride was added with irradiation and cooling with ice water to a solution of 3 g of *trans*-2,5-dimethyl-3-hexene-2,5-diol [1] in 80 ml of methylene chloride. After the usual treatment and crystallization from carbon tetrachloride we isolated 5.7 g of meso-3,4-dibromo-2,5-dimethyl-2,5-hexanediol, m.p. 82-83°. Found: C 31.60; 31.54; H 5.21; 5.40; Br 52.33; 52.62%. $C_8H_{16}O_2Br_2$. Calculated: C 31.60; H 5.30; Br 52.57%.

Bromination of *cis*-2,5-Dimethyl-3-hexene-2,5-diol

Under the above-indicated conditions 3 g of the *cis*-dimethylhexenediol [11] gave 6.1 g of oil (n_D^{20} 1.5212), which darkened on standing in air with elimination of hydrogen bromide. Found: C 31.72; 31.68; H 5.35; 5.44; Br 51.81; 51.90%. $C_8H_{16}O_2Br_2$. Calculated: C 31.60; H 5.30; Br 52.57%.

Effect of Additions of 2-Butyne-1,4-diol Diacetate and of 2-Butene-1,4-diol

Acetate on the Bromination of Toluene

Before the experiment streams of nitrogen were passed for 30 minutes through the toluene and the bromine. The reaction was carried out in a dark room illuminated with red light.

At 0° 1.8 g of bromine was added dropwise to 6 g of dry toluene, and there was a feeble evolution of hydrogen bromide. On the addition of 0.3 g of 2-butyne-1,4-diol diacetate an exothermic reaction started after a short time and was accompanied by a vigorous evolution of hydrogen bromide. The temperature of the mixture rose to 52° despite external cooling with ice water. After 50 minutes the mixture was washed with water and with thiosulfate and bicarbonate solutions; it was dried with calcium chloride and distilled. We obtained 6.6 g (82%) of benzyl bromide, b.p. 198-200° (752 mm).

When 0.3 g of 2-butene-1,4-diol diacetate was added to a mixture of bromine and toluene prepared under the above-indicated conditions, the temperature rose to 28°. The evolution of hydrogen bromide became more appreciable, but the bromination came to an end after only three hours, when a pale-yellow crystalline mass remained in the reaction vessel. The product was dissolved in ether, and the ether solution was washed with water and with a solution of sodium bicarbonate; it was dried with magnesium sulfate, and ether was vacuum-distilled off; the residue was dissolved in 10 ml of absolute alcohol and cooled to -35° with solid carbon dioxide in acetone. The precipitated crystals were rapidly filtered off. After recrystallization we obtained 5.2 g of *p*-bromotoluene, m.p. 26°. By cooling the mother liquor to -70° we isolated 1.7 g of *o*-bromotoluene, m.p. from -28° to -30°. Judging from its smell, the residue (1.3 g) contained benzyl bromide.

Kinetic Experiments

Reaction of the Diastereoisomeric Dibromides with Potassium Iodide. A mixture of 10 ml of a 0.03 M solution of the dibromide in methanol and 10 ml of a 0.25 M solution of potassium iodide in methanol was kept in a thermostat for 40 hours at 60°. The reaction mixture was then cooled with ice water, 5 ml of 10% hydrochloric acid was added, and the amount of iodine formed was determined by titration with 0.015 N sodium thiosulfate. The results (means of two parallel experiments) are given in Table 1.

Bromination Reaction. To 50 ml of a 0.1 M solution of the compound to be brominated in N,N-dimethylformamide was added rapidly 50 ml of a 0.1 M solution of bromine in N,N-dimethylformamide. During the mixing of the reagents the reaction flask was periodically lowered in a bath of cooling mixture so that the reaction temperature was kept at $25 \pm 3^\circ$. The mixture was then placed in a thermostat at 25°, and 1-ml samples were taken periodically by pipet. The reaction was stopped by adding the sample taken to 50 ml of 0.1 N HCl containing 1 g of potassium iodide, and the amount of iodine liberated was determined by titration with sodium thiosulfate solution. When the bromination was carried out in carbon tetrachloride, the procedure was similar, except that the reaction was stopped by adding the sample to 50 ml of alcohol containing 5 ml of concentrated hydrochloric acid and 1 g of potassium iodide. The results (means of two parallel experiments) are given in Table 2. All the experiments were carried out in a vessel made of dark glass and in a nitrogen atmosphere. Nitrogen was passed through the original solutions before the reaction for a period of 15 minutes.

SUMMARY

In the photochemical bromination of 2-butene-1,4-diol, its diacetate, and 2,5-dimethyl-3-hexene-2,5-diol in nonpolar solvents, trans-addition products are formed, whereas their acetylenic analogs give mainly cis-dibromides. The differences in the behavior of acetylenes and the corresponding olefins are to be explained on the view that under identical conditions they may react by different mechanisms. Thus, under given conditions 2-butyne-1,4-diol diacetate is brominated by a chain mechanism, whereas the corresponding olefin is brominated by a nonchain mechanism.

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*Original Russian pagination. See C. B. translation.

SYNTHESIS OF STEROIDS
AND RELATED SUBSTANCES

COMMUNICATION 49. SYNTHESIS OF STEROID ANALOGS
NOT CONTAINING A B RING

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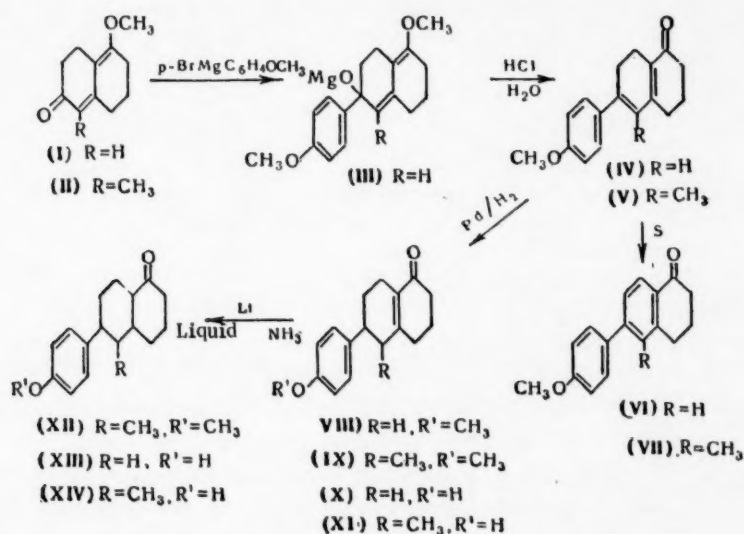
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We have shown previously [1, 2] that in the reaction of p-methoxyphenylmagnesium bromide with the bicyclic methoxy ketone (I) followed by decomposition of the product of the Grignard synthesis (III) with dilute hydrochloric acid the dienone (IV) is formed, and this on hydrogenation and demethylation gives the tricyclic steroid analogs (X) and (XIII). The latter products show estrogenic activity in tests on mice in doses of 4 and 3 mg respectively.

It was of interest to determine whether the above-indicated scheme is applicable in the preparation of 5-substituted derivatives of the type of (XI) and (XIV), the synthesis of which would afford the possibility of investigating the relation between estrogenic activity and structure in a series of steroid analogs not containing a B ring and would enable us to pass to a tetracyclic steroid by closure of the B ring if the 5-substituent is of the appropriate character.



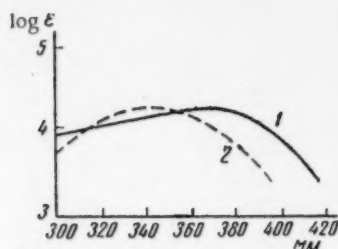


Fig. 1. Ultraviolet spectra: 1) (IV), λ_{\max} 368 (log ϵ 4.20); 2) (V), λ_{\max} 341 (log ϵ 4.197).

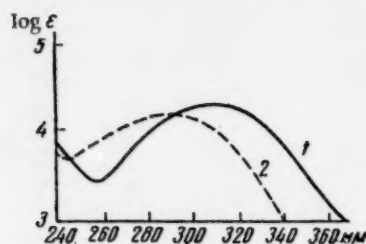


Fig. 2. Ultraviolet spectra: 1) (VI), λ_{\max} 308 (log ϵ 4.33); 2) (VII), λ_{\max} 288.5 (log ϵ 4.158).

As starting substance we took the previously described [3] bicyclic methoxy ketone (II), which, on reaction with *p*-methoxyphenylmagnesium bromide and subsequent hydrolysis gave 3,4,7,8-tetrahydro-6-*p*-methoxyphenyl-5-methyl-1(2H)-naphthalenone (V). The structure of the latter was confirmed by aromatization by heating it with sulfur, when it gave a derivative of 3,4-dihydro-1(2H)-naphthalenone (VII). The ultraviolet spectra of the dienone (V) and the dihydro-1(2H)-naphthalenone (VII) were found to be close to those of the corresponding derivatives (IV) and (VI) [4] (Figures 1 and 2), which do not contain a methyl group in the 5-position. On hydrogenation of the dienone (V) over palladium in alcohol, as in the case of homolog (IV) [2], selective reduction of the diene system occurred with formation of 3,4,5,6,7,8-hexahydro-6-*p*-methoxyphenyl-5-methyl-1(2H)-naphthalenone (IX), the position of the double bond in which was shown with the aid of the ultraviolet spectrum of the ketone itself (IX), which was analogous to the spectra of the ketone (VIII) (Fig. 3) and of the 2,4-dinitrophenylhydrazone of the ketone (IX). On reduction of the dienone (V) with lithium in liquid ammonia, it did not behave like its demethylated homolog (IV) [2], and the product was not the tricyclic unsaturated ketone (IX), but a compound of composition $C_{18}H_{22}O_4$. The reduction of the unsaturated ketone (IX) with lithium in liquid ammonia was analogous to that of (VIII) [2] and went normally with formation of octahydro-6-*p*-methoxyphenyl-5-methyl-1(2H)-naphthalenone (XII).

The demethylation of the methoxy ketones (IX) and (XII) by means of aluminum chloride in boiling xylene gave the corresponding phenols (XI) and (XIV), which by the action of dimethyl sulfate in an alkaline medium were reconverted into the original methoxy ketones (IX) and (XII). On the basis of the known fact regarding the steric orientation in the reduction of unsaturated ketones and taking account of the stability of the ketones (IX) and (XII) toward the action of alkoxides and aluminum chloride, we may assume that the methyl and methoxyphenyl groups of ketones (IX) and (XII) have *trans* positions and that the rings of the decalin system of the ketone (XII) are *trans* fused. The tricyclic phenols (XI) and (XIV) showed no estrogenic activity when tested on mice in doses of up to 6 mg.

EXPERIMENTAL *

Reaction of *p*-Methoxyphenylmagnesium Bromide with the Methoxy Ketone (II). A solution of 4 g of the methoxy ketone (II) [3] in 40 ml of ether was added to a stirred ice-cooled Grignard reagent prepared from 1.2 g of magnesium, 12 g of *p*-bromoanisole, and 40 ml of ether. After it had stood 12 hours at room temperature, the mixture was treated with ice and dilute hydrochloric acid; it was extracted with ether. The ether extract was washed with dilute alkali, hydrochloric acid, and water. After removal of solvent the residue was subjected to chromatography on alumina. Elution with benzene gave 1.8 g (33%) of the dienone (V), m.p. 76-77° (from isooctane). Found: C 80.49; H 8.28; 7.55%. $C_{18}H_{20}O_2$. Calculated: C 80.56; H 7.51%.

Its 2,4-dinitrophenylhydrazone had m.p. 188-189° (decomp.) (from methanol); λ_{\max} 420 mμ (alcohol). Found: N 12.83; 12.76%. $C_{24}H_{24}O_5N_4$. Calculated: N 12.50%.

Dehydrogenation of the Dienone (V). A mixture of 5 g of the dienone (V) and 1 g of sulfur was heated at 210-220° for 20 minutes. After chromatography on alumina (benzene) and treatment with semicarbazide, we

*L. F. Kudryavtseva took part in this work.

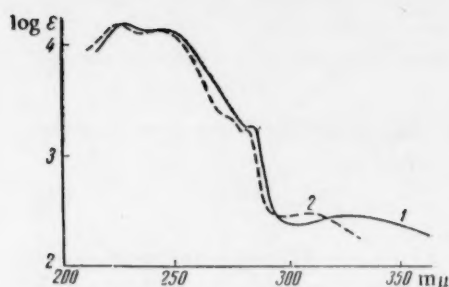


Fig. 3. Ultraviolet spectra: 1) (IX), λ_{\max} 228 (log ϵ 4.186); 245.5 (log ϵ 4.144); 284 (log ϵ 3.277); 331 (log ϵ 2.465); 2) (VII), λ_{\max} 227 (log ϵ 4.164); 244 (log ϵ 4.143); 284 (log ϵ 3.274); 311 (log ϵ 2.502).

isolated 3 g of a semicarbazone, m.p. 244-245°, which on decomposition with hydrochloric acid gave 1.5 g of 3,4-dihydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone (VII), m.p. 106-107° (from isooctane). Found: C 80.86; 80.96; H 6.56; 6.62%. $C_{18}H_{18}O_2$. Calculated: C 81.17; H 6.81%.

2,4-Dinitrophenylhydrazones: m.p. 235-237°; λ_{\max} 391 mμ (alcohol). Found: N 12.68; 12.80%. $C_{24}H_{22}O_5N_4$. Calculated: N 12.53%.

Reduction of the Dienone (V). 1. The dienone (V) (2.5 g) was hydrogenated in 100 ml of methanol in presence of palladium supported by calcium carbonate. In the course of six hours 250 ml of hydrogen was absorbed (19°, 746 mm). The catalyst was filtered off, and the methanolic solution was cooled with a mixture of acetone and solid carbon dioxide. There was a precipitate of 0.8 g (32%) of 3,4,5,6,7,8-hexahydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone (IX), m.p. 113-114° (from isooctane). The substance was unchanged after

standing for three days or after being heated for six hours with excess of potassium *t*-butoxide in *t*-butyl alcohol. Found: C 79.83; H 8.07; 8.19%. $C_{18}H_{22}O_2$. Calculated: C 79.96; H 8.20%.

2,4-Dinitrophenylhydrazones: m.p. 244-245° (from methanol); λ_{\max} 388 mμ (alcohol). Found: N 12.38; 12.51%. $C_{24}H_{26}O_5N_4$. Calculated: N 12.44%.

2. A solution of 1.7 g of the dienone (V) in a mixture of 25 ml of dioxane and 25 ml of ether was added to a solution of 1.2 g of lithium in 250 ml of liquid ammonia. After ten minutes the excess of lithium was decomposed with ammonium chloride, and the reaction mixture was poured into 500 ml of water. This gave 0.7 g of a substance of m.p. 183-184° (from methanol); λ_{\max} 243 and 227 mμ (alcohol). Found: C 71.52; 71.64; H 7.37; 7.44%. $C_{18}H_{22}O_4$. Calculated: C 71.50; H 7.33%.

Reduction of 3,4,5,6,7,8-Hexahydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone (IX). A solution of 0.6 g of 3,4,5,6,7,8-hexahydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone (IX) in a mixture of 15 ml of dioxane and 15 ml of ether was added to a solution of 0.3 g of lithium in 250 ml of liquid ammonia. After ten minutes the excess of lithium was decomposed with ammonium chloride, and after removal of ammonia the residue was treated with water and extracted with ether. This gave 0.5 g of an oil, which gave 0.4 g of the semicarbazone of octahydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone, m.p. 238-240° (decomp.) after being washed with hot methanol. Found: N 12.38; 12.44%. $C_{19}H_{27}O_2N_3$. Calculated: N 12.75%.

Decomposition of 0.4 g of this semicarbazone with dilute hydrochloric acid gave 0.1 g (17%) of octahydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone (XII), m.p. 117-118° (from isooctane). Found: C 78.92; 78.94; H 8.90; 8.74%. $C_{18}H_{24}O_2$. Calculated: C 79.30; H 8.88%. Its 2,4-dinitrophenylhydrazone had m.p. 204-206° (from methanol). Found: N 12.55; 12.64%. $C_{24}H_{28}O_5N_4$. Calculated: N 12.29%.

Demethylation of 3,4,5,6,7,8-Hexahydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone (IX). A mixture of 0.7 g of 3,4,5,6,7,8-hexahydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone (IX), 1.5 g of aluminum chloride, and 10 ml of xylene was refluxed for 7 minutes. When the reaction mixture had cooled, it was decomposed with ice and dilute hydrochloric acid. Extraction of the xylene layer with dilute potassium hydroxide solution and subsequent acidification with hydrochloric acid gave 0.45 g (68%) of 3,4,5,6,7,8-hexahydro-6-p-hydroxyphenyl-5-methyl-1(2H)-naphthalenone (XI), m.p. 185-187° (from aqueous methanol). Found: C 79.35; 79.47; H 7.61; 7.69%. $C_{17}H_{20}O_2$. Calculated: C 79.65; H 7.86%.

On methylation with dimethyl sulfate in an alkaline medium, as described previously [2], this hydroxy ketone was reconverted into the original methoxy ketone (IX).

Demethylation of Octahydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone (XII). A mixture of 0.2 g of octahydro-6-p-methoxyphenyl-5-methyl-1(2H)-naphthalenone (XII), 0.4 g of aluminum chloride, and 5 ml of xylene was heated at a bath temperature of 140-145° for seven minutes. When the mixture was cool, 5 ml of isooctane was added. There was a precipitate of 0.1 g (53%) of octahydro-6-p-hydroxyphenyl-5-methyl-1(2H)-naphthalenone (XIV), m.p. 182-184° (from aqueous methanol). Found: C 78.77; 78.89; H 8.32; 8.41%. $C_{17}H_{22}O_2$. Calculated: C 79.03; H 8.58%.

Its 2,4-dinitrophenylhydrazone had m.p. 193-194° (decomp.). Found: N 12.31; 12.39%. $C_{23}H_{26}O_5N_4$. Calculated: N 12.08%.

On methylation with dimethyl sulfate in an alkaline medium, this hydroxy ketone (XIV) was reconverted into the original methoxy ketone (XII).

In conclusion we thank I. A. Eskin and M. P. Danilova for testing the preparations for estrogenic activity, and we thank also V. M. Medvedeva for determining the ultraviolet spectra.

SUMMARY

3,4,5,6,7,8-Hexahydro-6-p-hydroxyphenyl-5-methyl-1(2H)-naphthalenone (XI) and octahydro-6-p-hydroxyphenyl-5-methyl-1(2H)-naphthalenone (XIV) were synthesized. These are structural analogs of estrone, but show no estrogenic activity in doses of up to 6 mg.

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TRANSFORMATIONS OF CYCLOALKENES OVER ALUMINUM SILICATES

COMMUNICATION 1. TRANSFORMATION OF CYCLOHEXENE INTO TETRAALKYLBENZENE AND DIMETHYLNAPHTHALENE HYDROCARBONS

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Various investigators have studied the catalytic transformations of cyclohexene. The isomerization of cyclohexene was first observed by Ynoue [1]. At 330° over Japanese clay cyclohexene is to a large extent converted into methylcyclopentenenes, which, as a result of the hydrogen-redistribution reaction, are then hydrogenated with formation of methylcyclopentane. These reactions were studied in greater detail over various catalysts by Zelinskii and Arbuzov [2]. It was thus shown that silica gel, alumina, and beryllia promote the isomerization of the six-membered ring into a five-membered ring, whereas chromic oxide, zirconia, divanadium trioxide, manganous oxide, and others bring about only the dehydrogenation of cyclohexene to benzene. Later Plate [3] showed that at 450-500° over a catalyst consisting of vanadium and aluminum oxides cyclohexene reacts in various ways. Among the reaction products he found methylcyclopentenenes, benzene, cyclohexane, methylcyclopentane, high-boiling aromatic hydrocarbons, and naphthalene. According to Frost's results [4], at a lower temperature (260°) over activated clay cyclohexene undergoes isomerization and polymerization reactions; the formation of benzene was not observed.

Bloch and Thomas [5] studied the transformations of cyclohexene in presence of a silica-alumina-thoria catalyst. At 200-300° isomerization was the main reaction. Raising the temperature to 400° favored the redistribution of hydrogen. The content of polymeric compounds in the catalyst varied from 20 to 40% on the raw material; the authors stated that these products consisted largely of aromatic hydrocarbons. In the 240-300° fraction they detected 2,6- and 1,6-dimethylnaphthalenes, and also some high-boiling naphthenes. An analogous investigation was carried out by Voge and co-workers [6] over a catalyst consisting of 86.2% of silica, 9.4% of zirconia, and 4.3% of alumina.

Yushkevich-Gavardovskaya, Lavrovskii, and others [7] treated cyclohexene over synthetic aluminum silicates at 450° at a pressure of 30 atm. Under these conditions the partial cracking of cyclohexene was accompanied by the formation of considerable amounts of coke and gas. The yield of catalyzate was about 82%. The monomeric fraction of the catalyzate contained not only methylcyclopentenenes and methylcyclopentane, but also products of destructive transformations. About 40% of the catalyzate consisted of high-boiling compounds containing alkylbenzenes, formed, in the opinion of the authors, by the alkylation of benzene obtained by the dehydrogenation of cyclohexene. Petrov and Shchekin [8] investigated the transformations of cyclohexene and 1-methylcyclopentene over an aluminum silicate at 250-316° at atmospheric pressure.

In addition to cyclohexene isomers the catalyzate contained high-boiling polymeric compounds, which according to the authors consisted of aromatic (methylphenylcyclopentane) and bicyclic naphthenes (cyclohexyl-methylcyclopentane). The amount of naphthalene hydrocarbons in the reaction products was not determined [9].

There is also a paper by Musaev and Shchekin [10] on the dehydration of cyclohexanol over aluminum silicates and the isomerization of the resulting cyclohexene.

In the investigations cited the monomeric fraction of the transformation products of cyclohexene was studied in some detail. The polymeric products obtained in the course of this process were not investigated, and the mechanisms of the reactions leading to their formation were not determined. The present paper reports the results of investigations on the catalytic transformations of cyclohexene over aluminum silicates.

EXPERIMENTAL

The cyclohexanol used in this work had b.p. 161-161.5°, d_4^{25} 0.9454; n_D^{25} 1.4640. The cyclohexene, obtained by the dehydration of cyclohexanol over alumina, had the following characteristics: b.p. 82-82.2°; d_4^{20} 0.8095; n_D^{20} 1.4474; iodine value 308.9. The transformations of cyclohexanol and cyclohexene were carried out at the optimum temperature of 350°, at a space velocity of 0.75:1, and at atmospheric pressure. The experiments were carried out in a continuous-flow reactor in a fluid bed of microspherical aluminum silicate catalyst. The experimental arrangement and apparatus were described previously [11].

The essential information on the process and the characteristics of the reaction products are given in Table 1. The results indicated that there was no essential difference in the compositions of the transformation products from cyclohexanol and from cyclohexene. The over-all yields of monomeric and polymeric fractions were 57-59% and 40-41%, respectively, on the hydrocarbon part of the catalyzate. However, the steam formed in the treatment of cyclohexanol suppressed the hydrogen-distribution reaction somewhat, which resulted in a relatively higher degree of unsaturation in the catalyzate. In the transformations of cyclohexanol and cyclohexene scarcely any gas formation was observed.

Most of the experimental work was carried out with cyclohexanol. The effects of temperature, rate of feed of starting material, pressure, etc., were studied. At temperatures up to 200° cyclohexanol was dehydrated over aluminum silicates without any appreciable reaction of the resulting cyclohexene. Further rise of temperature directed the process toward the isomerization and polymerization of cyclohexene and the hydrogen-redistribution reaction. It was shown that at 250° the main donor of hydrogen was the cokelike transformation products deposited on the catalyst. At 350° the dehydrogenation of polymeric products with formation of benzene and naphthalene hydrocarbons became of significance in the hydrogen balance. Use of pressure (5-10 atm) somewhat intensified the redistribution of hydrogen, which led to an increase in the yield of cokelike transformation products. The use of a vacuum (residual pressure of 250-100 mm) considerably suppressed the redistribution of hydrogen.

The catalytic transformations of cyclohexene over aluminum silicates are characterized by the simultaneous occurrence of isomerization, polymerization, and redistribution of hydrogen. The hydrogen donors in this process are the intermediate products that lead to the formation of coke and the hydrocarbons of the polymeric fraction. The study of the composition of the transformation products from cyclohexene has great scientific and practical importance. These investigations permit an examination of the redistribution of hydrogen in the course of the complex process and the determination of the extent to which the polymeric products participate in the hydrogen balance of the process.

The catalyzates obtained under optimum conditions were fractionated into monomeric and polymeric fractions, which were then subjected to spectrum and chemical investigations.

Monomeric Product. The monomeric fraction, whose main properties are given in Tables 2 and 3, boiled over the range 46-110°. Its content of unsaturated hydrocarbons was 18%. About 76% of the product was accounted for by the 70-73° fraction. The main fractions of the monomeric product were subjected to Raman-spectrum investigation. The results showed that the 70-73° fraction consisted mainly of methylcyclopentane (> 90%), small amounts of 1-methylcyclopentene and 4-methylcyclopentene, and traces of 2-methylcyclopentene. On the basis of iodine values, the total content of unsaturated hydrocarbons in this fraction was 8%. In the 73-79° fraction we detected methylcyclopentane (20-25%), 1-methylcyclopentene (20-25%), 4-methylcyclopentene (15-20%), cyclohexene (5-7%), cyclohexane (20-25%), and traces of 2-methylcyclopentene. The total content of unsaturated compounds was 52%. The 79-110° fraction (yield about 4%) did not differ appreciably from the preceding fraction; its iodine value was 150.7, and the content of unsaturateds was about 50%. Hence, the monomeric fraction consisted to the extent of more than 90% of a mixture of methylcyclopentane and methylcyclopentenes; its cyclohexane-cyclohexene content was less than 10%.

TABLE 1

Characteristics of Products of the Transformation of Cyclohexene

Characteristic of product	Cyclohexanol		Cyclohexene	
	yield of fraction (% by wt)	n_D^{20}	yield of fraction (% by wt)	n_D^{20}
Fractional Composition:				
Start of boiling (°C)	66,0		44,5	
Start of boiling to 70	3,72	1,4041	4,64	1,4015
70—73	44,76	1,4109	44,42	1,4117
73—79	6,66	1,4158	3,29	1,4195
79—85	3,26	1,4266	2,83	1,4232
85—100	0,46	1,4301	1,91	1,4232
100—110	0,30	1,4320	—	—
Yield of fraction boiling up to 110° (% by wt)	59,46		57,09	
Residue (% by wt)	40,0		41,25	
Losses (% by wt)	0,84		1,66	
Refractive index n_D^{20}	1,4609		1,4558	
Sp. gr. d_4^{20}	0,8287		0,8149	
Iodine value	40,0		25,3	
Mol. wt.	103,0		104,6	
Unsaturated hydrocarbons (% by wt)	16,1		10,4	
Sulfonatability (% by vol.)	43,2		36,5	
Material Balance (% by wt):				
Hydrocarbons	77,1		90,0	
Water	17,4		—	
Coke	3,6		4,5	
Gas	—		—	
Losses	1,9		5,5	
Fraction of b.p. 70—73°:				
Yield of fraction (% by wt)	44,76		44,42	
n_D^{20}	1,4109		1,4117	
d_4^{20}	0,7480		0,7496	
Iodine value	30,2		13,2	
Residue (> 110°):				
Amt. of residue (% by wt)	40,0		41,25	
n_D^{20}	1,5381		1,5318	
d_4^{20}	0,9334		0,9231	
Sulfonatability (% by wt)	80,7		79,1	
Iodine value	41,6		31,2	
Mol. wt.	147,0		146,1	
Unsaturated hydrocarbons (% by wt)	24		17,9	

The results given above show that in the catalytic treatment of cyclohexene over aluminum silicates about 55% of it is isomerized into methylcyclopentenenes, which in the hydrogen-redistribution process is converted mainly into methylcyclopentane.

Polymeric Product. As already stated about 40% of polymeric products was formed in the course of the catalytic treatment of cyclohexene. The polymeric product isolated from the catalyzate boiled mainly in the range 190–300° and had: d_4^{20} 0.9277; n_D^{20} 1.5287; mol. wt. 153.4; iodine value 37.4; sulfonatability 82.4%. The characteristics of the main fractions of the polymeric product are given in Table 4. The total yield of products boiling up to 190° was only 6.3%. This fraction was characterized by a relatively low content of aromatic hydrocarbons (about 36%).

The 190–210° fraction (yield 6.3%) contained about 28% of aromatic hydrocarbons. Its content of unsaturated compounds was 14.4%. The 210–220° fraction distilled over to an extent of more than 95% in a range of three degrees (214–217°) and had a comparatively low content of unsaturated compounds (4.9%). The main component of this fraction consisted of naphthenes. Its content of aromatics was 36.5%. The naphthene part of the fraction had the following characteristics: d_4^{20} 0.8642; n_D^{20} 1.4672; mol. wt. 165.2; aniline point 54°; elementary analysis showed that it contained 86.9% of carbon and 13.1% of hydrogen, which corresponds to decahydridimethylnaphthalene (C 86.7%, H 13.3%). MR calculated 53.0; MR found 53.09. The Raman spectrum of the product was

TABLE 2

Characteristics of the Monomeric Fraction of the Catalytic-transformation Products from Cyclohexene (atmospheric pressure, 350°, space velocity 0.75:1)

Characteristic of product	Yield of fraction (% by wt)	n_D^{20}
Start of boiling (°C)		46
to 70	2,29	1,4082
70-73	75,86	1,4112
73-79	14,81	1,4254
79-85	1,05	1,4391
85-110	2,74	1,4292
End of boiling	110	
Total yield (% by wt)	96,75	
Residue	1,71	
Losses	1,54	
d_4^{20}	0,7553	
n_D^{20}	1,4139	
Iodine value	56	
Mol. wt.	82,8	
Unsaturated hydrocarbons (% by wt)	17,8	

TABLE 3

Characteristics of the Main Fractions of the Monomeric Product

Characteristic of fraction	Value
Fraction of b.p. 70-73°	
Yield of fraction (% by wt)	75,86
n_D^{20}	1,4112
d_4^{20}	0,7491
Iodine value	24,6
Fraction of b.p. 73-79°	
Yield of fraction (% by wt)	14,81
n_D^{20}	1,4254
d_4^{20}	0,7724
Iodine value	162,2
Fraction of b.p. 79-110°	
Yield of fraction (% by wt)	3,79
n_D^{20}	1,4319
d_4^{20}	0,8027
Iodine value	150,7

The values of d_4^{20} and n_D^{20} for the fractions increased progressively. The amount of unsaturated hydrocarbons varied in the range 12-21%. The average molecular weight of

investigated and compared with the spectra of pure decalin isomers [12] and with a list of the characteristic frequencies of decalin derivatives [13]. This comparison showed that the spectrum of the sample contained all of the most intense lines of compounds of the decalin structures. Hence, the product investigated consisted mainly of hydrocarbons of decalin structure with a considerable predominance of trans isomers (decahydrodimethylnaphthalenes).

In degree of unsaturation the 220-225° fraction scarcely differed from the preceding fraction. Its aromatics content was 45%. In the fractions coming over in the range 225-250° there was a sharp qualitative change in the product which was associated with a considerable increase in the content of aromatic hydrocarbons (60-80%) and a corresponding decrease in the amount of naphthenes.

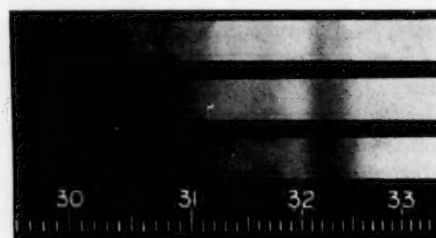


Fig. 3. Absorption spectra of fractions of boiling range: 1) 240-250°; 2) 250-260°; 3) 260-270° (along the axis of abscissae is the wavelength scale of the spectrograph: each unit = $1 \cdot 10^{-6}$ mm).

TABLE 4

Characteristics of Polymeric Fraction (atmospheric pressure, 350°, space velocity 0.75:1)

Boiling range (°C)	Yield of fraction (% by wt)	n_D^{20}	d_4^{20}	Iodine value	Mol. wt.	Sulfonatabi- lity (% by vol.)
Up to 190°	6,32	1,4557	0,8311	33,5	115,3	46
190—210	6,32	1,4782	0,8664	24,5	151,0	39,7
210—220	15,89	1,4841	0,8813	8,1	154,8	39,3
220—225	6,52	1,4943	0,8955	9,2	152,6	49,2
225—230	9,13	1,5071	0,9108	20,0	152,4	75,0
230—235	8,10	1,5198	0,9227	28,0	152,3	92,0
235—240	5,62	1,5259	0,9325	23,6	153,3	94,6
240—250	7,21	1,5363	0,9416	36,1	149,5	97,5
250—260	8,74	1,5763	0,9751	53,5	150,6	100
260—270	11,22	1,5968	0,9923	50,4	151,8	100
270—280	1,63	1,5955	0,9933	45,2	152,0	100
280—300	2,50	1,5775	0,9823	42,9	152,5	100

Start of boil, 78.5°C; end of distillation, 300°C; total yield, 89.2%; residue, 9.25%; losses, 1.55%.

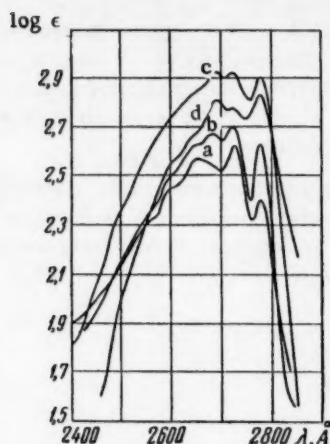


Fig. 1. Ultraviolet absorption spectra of alkylbenzene fractions of boiling range: a) 190-210°; b) 210-220°; c) 220-225°; d) 225-230°.

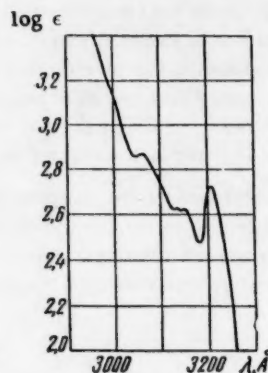


Fig. 2. Ultraviolet spectrum of fractions of boiling range 260-270°.

high contents of alkylnaphthalenes. The specific gravities and refractive indices of the fractions varied in the ranges 0.972-0.993 and 1.576-1.597, respectively.

Alkylbenzene and alkylnaphthalene hydrocarbons present in the polymeric product from cyclohexene were studied with the aid of the ultraviolet absorption spectra. The absorption spectra were investigated with the aid of a quartz spectrograph and photoelectric spectrophotometer. The fractions were investigated in isooctane solution in concentrations of $1 \cdot 10^{-3}$ – $1 \cdot 10^{-4}$ mole/liter. The main characteristics of the narrow fractions are given in Table 4. Fig. 1 gives the absorption spectra of fractions boiling in the range 190-240°.

The general character of these spectra indicate that the fractions consisted mainly of alkylbenzenes [14-16]. The 190-210° fraction contained, as its main aromatic components, tetraalkylbenzenes with the substituents in the 1,2,3,5- and 1,2,3,4-positions and a very small amount of the 1,2,4,5-isomer. In addition, m- and p-dialkylbenzenes were shown to be present. The 210-220° fraction was similar in composition. It was shown that the 220-225° fraction contained the same components. The 230-235° fraction consisted mainly of 1,2,4,5-tetraalkylbenzenes, but there was also a certain amount of p-dialkylbenzenes and small amounts of other tetra-

the five-degree fractions was 150-152. Fractions coming over above 250° differed considerably in composition from the preceding fractions, which was associated with their

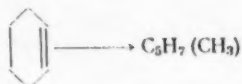
alkylbenzenes. The 225-230° and 235-240° fractions were similar in composition, though traces of naphthalene hydrocarbons were detected in the latter.

In the spectra of the subsequent fractions, which boiled in the range 240-270°, the benzene region was already completely blotted out by the intense band associated with naphthalene hydrocarbons. In the spectra of all fractions containing naphthalenes the absorption maxima shown in Fig. 2 were found in the 2900-3300 Å range. Fig. 3 presents a photograph of the absorption spectra of the 240-250°, 250-260°, and 260-270° fractions, which confirms that in these fractions the naphthalene hydrocarbons present are the same in character [17]. On the assumption that the content of naphthalenes in the 260-270° fraction could be taken as 100%,* the amounts of naphthalenes in the 240-250° and 250-260° fractions were calculated.

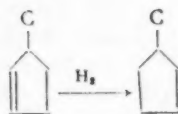
It was thus shown that the 240-250° fraction contained $13 \pm 1\%$ of naphthalenes and the 250-260° fraction contained $49 \pm 1\%$ of naphthalenes. The results of these investigations showed that the main component of fractions boiling in the range 240-270° was 1,2-dimethylnaphthalene, and there was also a little 2,6-dimethylnaphthalene. It is possible that there was also some 1,3-dimethylnaphthalene. In the residual fraction, which boiled above 300°, we detected di- and tri-substituted naphthalenes and a very small amount of tricyclic aromatic hydrocarbons.

The 225-230° and 230-235° fractions of the polymeric product, which consisted mainly of tetraalkylbenzenes (according to the ultraviolet spectra), were investigated also with the aid of their Raman spectra. The results of these analyses showed that the fractions under investigation consisted mainly of a mixture of the above-indicated tetraalkylbenzenes (also dimethyl- and diethyl-benzenes). It was shown that these products also contained a small amount of hydrocarbons of the decalin series. The 260-270° fraction, which consisted mainly of naphthalene hydrocarbons, was investigated by the picrate method [18]. On treatment of this fraction with picric acid there was a copious precipitate of bright-orange picrates. On cooling, the product turned completely into a solid mass of picrates. The melting point of the picrate obtained was 105.5°. These results also confirm that the fraction under investigation was a mixture of isomeric dimethylnaphthalenes.

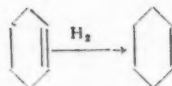
The results obtained on the compositions of the monomeric and polymeric products of the transformation of cyclohexene enable us to propose the following scheme of the most probable reactions in the catalytic treatment of cyclohexene over aluminum silicates. In the formation of the hydrocarbons of the monomeric fraction the isomerization of cyclohexene into methylcyclopentenes is of great importance;



This is followed by the hydrogenation of methylcyclopentenes into methylcyclopentane:



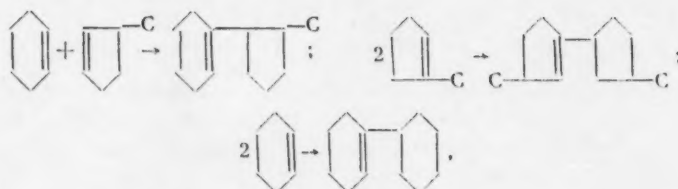
Some of the original cyclohexene is hydrogenated with formation of cyclohexane:



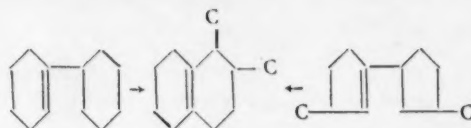
The polymeric fraction, as stated above, was a mixture of alkylbenzenes, alkyl-naphthalenes, and some naphthalenes. It contained also some unsaturated compounds.

*The values of $\log \epsilon$ for the absorption maxima in the spectrum of the 260-270° fraction corresponded to the values of $\log \epsilon$ for individual hydrocarbons.

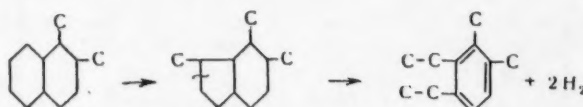
The formation of these hydrocarbons structures evidently occurs via the formation of the dimer of methylcyclopentene or cyclohexene by the reactions



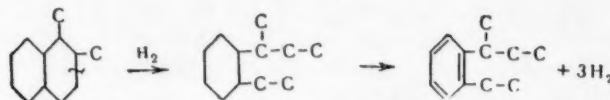
and this then isomerizes into the corresponding hydrocarbons of decalin or octalin structure



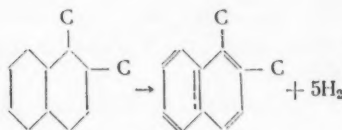
Such isomerization was observed by Zelinskii [19], Huckel [20], Plate [21], and others. It must be assumed that the formation of tetraalkylbenzenes, e.g., 1,2-diethyl-3,4-dimethylbenzene, results from isomerization followed by the hydrogenolysis of one of the rings of decahydrodimethylnaphthalene and dehydrogenation of the resulting monocyclic hydrocarbon:



The dialkylbenzenes contained in the polymeric product are formed as a result of an analogous transformation of decahydro- or octahydro-dimethylnaphthalene:



The fraction boiling in the range 260-280° consisted mainly of a mixture of dimethylnaphthalenes with a predominance of 1,2-dimethylnaphthalene, which was formed by the dehydrogenation of decahydro-1,2-dimethylnaphthalene:



The resulting 1,2-dimethylnaphthalene underwent partial isomerization with formation of other dimethylnaphthalenes.

It is probable also that the conversion of cyclohexene into aromatic and naphthalene hydrocarbons proceeds partly through the intermediate stage of a hydrogenated analog of cyclobutadibenzene, which, over aluminum silicates under the given conditions undergoes isomerization, dehydrogenation, and hydrogenolysis with formation, as final products, of the above-stated tetraalkylbenzenes (mainly the 1,2,4,5-isomers) and dimethylnaphthalenes. This course, however, is hypothetical and requires further study. The relatively small amount of unsaturated compounds in the polymeric products evidently consists of incompletely dehydrogenated analogs of decalin hydrocarbons and other alkylcycloalkenes formed as intermediate products in the course of the conversion of decahydrodimethylnaphthalene into tetraalkylbenzene and dimethylnaphthalene hydrocarbons. As already established

[22-24], the products of pyrolysis and of thermal and catalytic cracking contain appreciable amounts of six- and five-membered cycloalkenes. The results of the investigation give reason to suppose that in thermocatalytic treatments of petroleum products the transformations of unsaturated cyclic compounds which we have established in this work are, together with other aromatization reactions, of great importance.

SUMMARY

1. A study was made of the catalytic transformations of cyclohexene over aluminum silicates.
2. At 300-350° at atmospheric pressure, about 60% of the cyclohexene is isomerized into methylcyclopentenes, which are then partially hydrogenated to methylcyclopentane. About 40% of the cyclohexene is dimerized, and the dimer is isomerized into hydrocarbons of the decalin and octalin series; subsequent isomerization, hydrogenolysis, and dehydrogenation of these lead to the formation of tetraalkylbenzenes and dialkyl-naphthalenes as end products.
3. On the basis of the study of the transformations of cyclohexene it is suggested that in the processing of petroleum products over aluminum silicates, together with other aromatization reactions, the transformations of unsaturated cyclic compounds play an important part.
4. Of the hydrogen consumed in the course of the transformations of cyclohexene, 50-55% is accounted for by the polymeric compounds transformed in the process into aromatic and naphthalene hydrocarbons, and 45% is accounted for by coke-forming condensation products.

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*Original Russian pagination. See C. B. translation.

CATALYTIC ALKYLATION OF TETRALIN

COMMUNICATION 1. ALKYLATION OF TETRALIN WITH C₅ OLEFINS

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Alkyltetralins [alkyl-1,2,3,4-tetrahydronaphthalenes] are prepared by the cyclization of aromatic compounds [1] and with the aid of the Grignard reaction [2]. For this purpose tertiary alcohols are prepared from 3,4-dihydro-1(2H)-naphthalenone (or 3,4-dihydro-2(1H)-naphthalenone) and alkyl bromides, and these are dehydrated to the corresponding unsaturated hydrocarbons, the hydrogenation of which gives alkyltetralins. Alkyltetralins can be prepared also by the hydrogenation of alkyl-naphthalenes [3], by the Friedel-Crafts reaction [4-7], and finally by the alkylation of tetralin with olefins [8-10] and with alcohols [8, 11].

The preparation of alkyltetralins by alkylation is a one-stage process and therefore merits the greatest attention. However, there have been very few investigations in this field. Ethyltetralin and diethyltetralin were prepared by the alkylation of tetralin with ethylene in presence of 85% phosphoric acid. The reaction was carried out in an autoclave at 300° [10], and only 5% of the tetralin was alkylated. By the alkylation of tetralin with ethylene in presence of an aluminum silicate catalyst at 300° and elevated pressure, monoethyltetralin [8] was obtained in about 15% yield. By the alkylation of 132 g of tetralin with propene in presence of hydrofluoric acid at 5-15°, 136 g of a wide fraction, b.p. 136-270° (4.6 mm), was obtained [9]. Tatarenko and Tsukervanik [11] studied the alkylation of tetralin by C₅ alcohols in presence of AlCl₃, ZnCl₂, and H₃PO₄. In some experiments the yield of alkyltetralins reached 82%.

In the present work we studied the alkylation of tetralin with amylenes (C₅ olefins) in the vapor phase. In presence of zinc chloride supported on alumina at 300-350° tetralin was dehydrogenated with formation of naphthalene, the yield of which attained 48.5%. Catalysts prepared by the impregnation of alumina with phosphoric acid solution were also found to be of low activity for the alkylation of tetralin. More satisfactory results were obtained in presence of synthetic and industrial aluminum silicate catalysts at 200° and 40 atm (the pressure was created by the vapors of the reactants and the introduction of nitrogen). The yield of the amyltetralin fraction, boiling range 155-168° (7 mm),* was then 12.9% on the amylenes and 25.9% on the tetralin taken. The tetralin that did not react remained unchanged and was used for further alkylation.

EXPERIMENTAL

The original tetralin boiled at 206-206.5° (748 mm) and had n_D^{20} 1.5425 and d_4^{20} 0.9712 [12]. The mixture of amylenes taken for the alkylation boiled in the range 20-35° and was prepared by the dehydration of isopentyl alcohol at 280° in presence of alumina. In the experiments on the alkylation of tetralin with amylenes the following catalysts were investigated: zinc chloride on alumina (30% ZnCl₂) (Catalyst 1); alumina impregnated with phosphoric acid (10% and 20%) (Catalysts 2 and 3); synthetic aluminum silicate catalyst containing

*According to the literature [2, 11], at atmospheric pressure amyltetralins boil in the range 275-289°.

TABLE 1

Alkylation of Tetralin in Presence of Catalyst 5 (industrial aluminum silicate)¹

Expt.	Temp. (°C)	Pressure (atm)	Amt. of amylenes (g)	Molar ratio of tetralin to olefin	Yield (g) of fraction	
					of b.p. 155-168° (7 mm)	of b.p. above 168° (7 mm)
1	300	1	17,5	1 : 1	7,0	1,5
2	250	1	17,5	1 : 1	6,3	1,7
3	300	20	17,5	1 : 1	6,0	1,0
4	250	20	17,5	1 : 1	6,5	1,5
5	250	10	17,5	1 : 1	6,0	3,0
6	250	40	17,5	1 : 1	7,0	2,3
7	250	40	35	1 : 2	12,5	6,3
8	200	40	35	1 : 2	13,1	8,5
9	200	40	35	1 : 2	13,0	5,0

aluminum silicate catalyst of composition 85.35% SiO₂, 11.91% Al₂O₃, 0.15% Fe₂O₃; 0.44% CaO; 0.63% MgO; 1.07% SO₃, and 0.021% Na₂O (Catalyst 5).

The alkylation was carried out in a flow system at atmospheric and elevated pressures in an atmosphere of nitrogen. In each experiment we took 0.25 mole (33 g) of tetralin in the amylene mixture in the amount shown in Table 1. The mixture was passed at a space velocity of 0.2 hr⁻¹ at atmospheric pressure and 0.5 hr⁻¹ at pressure of 10, 20, and 40 atm. When the amylene fraction had been distilled off, the catalyzate was distilled at 7 mm through a column of 15-plate efficiency.

When a mixture of tetralin and amylenes was passed over Catalyst 1 at 250°, 300°, and 350°, the dehydrogenation of tetralin to naphthalene was observed. In presence of Catalysts 2 and 3 at 300° the alkylation, as well as dehydrogenation, of tetralin was observed. From the combined catalyzates obtained in experiments at elevated pressure, some amyltetralin [b.p. 284-286° (746 mm); n_D²⁰ 1.5335; d₄²⁰ 0.9497] was isolated, but in only 5% yield. The alkylation of tetralin with amylenes over Catalyst 5 was carried out at tetralin: amylene molar ratios of 1 : 1 and 1 : 2 at various temperatures and pressures. The yield of the amyltetralin fraction, b.p. 155-168° (7 mm), was then 12.9% on the amylene taken and 25.9% on the tetralin (see Table 1, Expt. 8).

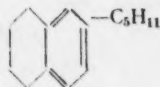
The alkylation of tetralin with amylenes over Catalyst 4 was carried out at 200° under a nitrogen pressure of 40 atm (Table 2). From Table 2 it will be seen that in the alkylation of tetralin with amylenes over Catalyst 4 the yield of the amyltetralin fraction, b.p. 155-168° (7 mm) attained 18.1% (Expt. 3). The combined fractions of b.p. 155-168° (7 mm) obtained in the alkylation of tetralin with amylenes in presence of an industrial aluminum silicate catalyst were distilled through a column of 40-plate efficiency at 2 mm. From 80 g of this fraction we isolated 70.2 g of amyltetralin, which came over at 110° and had: n_D²⁰ 1.5330; d₄²⁰ 0.9493; Found MR 66.07; C₁₅H₂₂F₃. Calculated MR 65.67. Found: C 89.13; 89.31; H 10.53; 10.70%. C₁₅H₂₂. Calculated: C 89.04; H 10.96%.

TABLE 2

Alkylation of Tetralin with Amylenes over Catalyst 4 (synthetic aluminum silicate)

Expt.	Amt. taken (g)		Molar ratio of tetralin to olefin	Space ve- locity (hr ⁻¹)	Yield (g) of fraction	
	of tetra- lin	of amy- lenes			of b.p. 155-168° (7 mm)	of b.p. above 168° (7 mm)
1	33,0	17,5	1 : 1	0,5	8,6	2,3
2	33,0	17,5	1 : 1	0,25	9,0	3,5
3	66,0	35,0	1 : 1	0,25	18,3	16,2
4	66,0	17,5	2 : 1	0,25	12,0	7,5

For "x-pentyltetralin" the literature [13] gives: b.p. 147-150° (12 mm); d_4^{20} 0.9478; n_D^{20} 1.5332. The infrared spectrum of the vibration overtones of the amyltetralin that we obtained resembled the spectrum of a 1,2,4-trialkylbenzene in the 5-6 μ region; the product can therefore be regarded as a β -amyltetralin:



By fractionation through a column of 15-plate efficiency at 3 mm, from 20 g of combined fractions of b.p. above 168° (7 mm) we isolated 5.5 g of a fraction having boiling range 132-135°, n_D^{20} 1.5525; d_4^{20} 0.9535. This fraction appeared to consist of a mixture of amyl-naphthalene and amyltetralin. The remaining 15 g of material boiled over a wide range (200-300°) and appeared to consist of a mixture of products of the further alkylation of tetralin and naphthalene together with polymers of the amylenes.

The infrared spectra were determined by V. A. Shlyapochnikov, to whom the authors express their thanks.

SUMMARY

1. It was shown that tetralin can be alkylated with amylenes over an aluminum silicate catalyst at 200-250° under a pressure of nitrogen of 40 atm.
2. Under these conditions β -amyltetralins are formed in a yield of 12.9% on the amount of amylenes used and 25.9% on the amount of tetralin taken for one passage.

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ACETYLENE-DIENE ISOMERIZATION OF
1,4-DICHLORO-2-BUTYNE AND SYNTHESIS BASED ON IT
COMMUNICATION 1. ACTION OF AQUEOUS-METHANOLIC
AND METHANOLIC SOLUTIONS OF POTASSIUM HYDROXIDE
ON 1,4-DICHLORO-2-BUTYNE

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The theoretical interest associated with the chemistry of butadiyne and, in particular, with 1-buten-3-ynyl ethers prompted investigations in this field in our laboratory, and some of these have already been published [1-4]. The butadiyne required for the syntheses was prepared by known methods of effecting the dehydrochlorination of 1,4-dichloro-2-butyne published in a German patent [5] and in a paper by Herbertz [6].

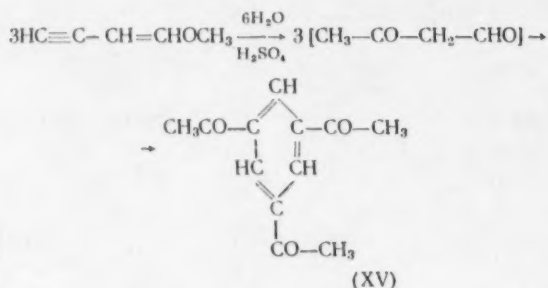
No explanation has yet been given in the literature of the mechanism of the dehydrochlorination of 1,4-dichloro-2-butyne to butadiyne under the action of aqueous-alcoholic alkali. Skvarchenko [7] noted that, in its reaction with alkylmagnesium halides, 1,4-dichloro-2-butyne may react in the form of its diene isomer 2,3-dichloro-1,3-butadiene, and this was confirmed by the isolation from the products of reaction with methylmagnesium bromide of two isomeric hydrocarbons corresponding to 3-hexyne and 2,3-dimethyl-1,3-butadiene, though under the usual conditions, as Johnson pointed out [8], it is not possible to find double bonds in 1,4-dichloro-2-butyne with the aid of the Raman spectrum. We oxidized 1,4-dichloro-2-butyne with permanganate and obtained chloroacetic acid as the only reaction product.

On the assumption that in the dehydrochlorination of 1,4-dichloro-2-butyne under the action of alcoholic potassium hydroxide the elimination of hydrogen chloride from one and the same carbon atom is improbable, we attempted to establish the occurrence of isomerization by examination of the reaction products. Of the products of the reaction of methanolic or aqueous-methanolic potassium hydroxide with 1,4-dichloro-2-butyne (I) we succeeded in isolating and characterizing various compounds: 2-chloro-1-buten-3-yne (IV), 2-chloro-4-methoxy-1,3-butadiene (V), butadiyne (VI), 1-methoxyl-1-buten-3-yne (VII), and tetrolaldehyde dimethyl acetal (VIII); these can be envisaged as arising from 1,4-dichloro-2-butyne when the isomerization of the latter into 2,3-dichloro-1,3-butadiene (III) via 3,4-dichloro-1,2-butadiene (II) is assumed.

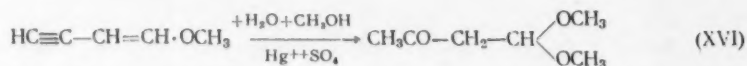
When 1.5 moles of potassium hydroxide as an aqueous-methanolic solution was added dropwise to 1 mole of 1,4-dichloro-2-butyne as a methanolic solution at 58-60°, then after a short time not only butadiyne, but also 2-chloro-1-buten-3-yne (IV) could be isolated. When about 2 moles of potassium hydroxide as a methanolic solution was added to the same amount of 1,4-dichloro-2-butyne without passage of nitrogen at about 60°, then 2-chloro-4-methoxy-1,3-butadiene (V) could be isolated from the reaction products. The use of a large amount of alkali and rise in the reaction temperature to 65° gave mainly the 1-buten-3-ynyl ether (VII) and butadiyne (VI). Under severer reaction conditions, tetrolaldehyde dimethyl acetal (VIII) was obtained. We observed also the addition of methanol to 1,4-dichloro-2-butyne in presence of potassium hydroxide at below 50°. This gave a product of the addition of methanol containing two chlorine atoms in the molecule, possibly a 1-methoxy-2,3-dichlorobutene; the investigation of this compound will be published separately.



Under the action of 10% sulfuric acid 1-methoxy-1-buten-3-yne is converted into triacetylbenzene (XV), which differs from Herbertz's results, according to which 3-butyral is obtained under these conditions. We explain the formation of triacetylbenzene by the hydration and hydrolysis of 1-methoxy-1-buten-3-yne and the condensation of the resulting unstable acetoacetaldehyde:



By the hydration of 1-methoxy-1-buten-3-yne (VII) in aqueous methanol in presence of mercuric sulfate we obtained acetoacetaldehyde dimethyl acetal (XVI):



The same acetal was obtained by the hydration of tetrolaldehyde dimethyl acetal (VIII) under the same conditions. The 1,4-dichloro-2-butyne required for the investigations was prepared by the action of thionyl chloride on 2-butyne-1,4-diol; the procedure differed from that described in the literature in that the isolation of 1,4-dichloro-2-butyne from the reaction products was effected by steam distillation.

EXPERIMENTAL

Preparation of 1,4-Dichloro-2-butyne (I). A 1500-ml flask fitted with mechanical stirrer, dropping funnel, and thermometer was charged with 430 g (5 moles) of 2-butyne-1,4-diol purified by vacuum distillation [m.p. 56.58°, b.p. 140-142° (12 mm)] and 5 ml of pyridine, and the mixture was cooled with ice and salt and stirred while 1400 g (850 ml) of thionyl chloride was added from a dropping funnel at such a rate that the temperature inside the flask was kept at from -10° to -20°. When the whole of the thionyl chloride had been added, mechanical stirring was continued for 2-3 hours and the mixture was left without stirring for 10-12 hours with the application of cooling so that in this time the temperature did not rise above 10°. The flask was then warmed to remove sulfur dioxide; the temperature inside the flask was gradually raised to 60-65°, when the liberation of sulfur dioxide stopped; 50 ml of water was then added to decompose unchanged thionyl chloride, and the mixture was steam-distilled. We obtained 570 g of crude 1,4-dichloro-2-butyne and about 2 liters of aqueous distillate, which was shaken with 100 ml of diethyl ether. The ether extract was combined with crude 1,4-dichloro-2-butyne and was dried with calcium chloride. Distillation under the vacuum of a water pump gave 540 g (87.9%) of a substance of b.p. 70-71° (23-24 mm). It had b.p. 60° (10 mm); 67° (20 mm); 75° (30 mm); 82° (40 mm); 165-166° (760 mm); d_4^{20} 1.2606; n_D^{20} 1.5060.

Raman-spectrum investigation of the 1,4-dichloro-2-butyne that we prepared showed the presence of frequencies corresponding to the triple bond and the complete absence of frequencies corresponding to a double bond.

Oxidation of 1,4-Dichloro-2-butyne with Permanganate. A flask fitted with mechanical stirrer, thermometer, and dropping funnel was charged with 30.75 g (0.25 mole) of 1,4-dichloro-2-butyne, and with cooling with ice and salt and stirring gradual addition of 80 g of potassium permanganate was made at such a rate that the temperature inside the flask was kept between -5° and +5°. The solution was filtered from the precipitate of manganese dioxide and evaporated to 200-250 ml. To the residue we added 100 ml of 50% sulfuric acid, and chloroacetic acid was extracted by shaking the mixture in a separating funnel with three 100-ml portions of ether. The combined ether extracts were dried with calcium chloride, ether was distilled off, and the residue was distilled from a Wurtz flask through an air condenser. We obtained 34.5 g (72.8%) of chloroacetic acid, m.p. 62-63° and b.p. 184-185°. A mixture with known chloroacetic acid showed no depression of melting point.

Action of Methanolic Potassium Hydroxide on 1,4-Dichloro-2-butyne. Formation of 2-Chloro-1-buten-3-yne (IV) and Butadiyne (VI). A mixture of 122.9 g (1 mole) of 1,4-dichloro-2-butyne, 200 ml of methanol, and 1 ml of pyridine was prepared in a 1-liter flask fitted with mechanical stirrer, thermometer, dropping funnel, tube for passage of nitrogen, and water-cooled condenser set for distillation and connected to a receiver which, in its turn, was connected to a trap cooled with solid carbon dioxide; with stirring at 58-60° in a stream of nitrogen dropwise addition was made of a solution of 90 g of potassium hydroxide in a mixture of 200 ml of water and 100 ml of methanol over a period of one hour. In the course of this time 50 ml of a mixture of methanol, 2-chloro-1-buten-3-yne (IV), and butadiyne (VI) dropped into the receiver. Water (200 ml) was added to the distillate, the aqueous methanol layer was separated; the upper layer was dried with calcium chloride and distilled. This gave 18 g of butadiyne, m.p. -35°, and 1.5 g of a substance of b.p. 63-65° (760 mm); d_4^{20} 1.030; n_D^{20} 1.4697; Found MR 23.17; Calculated MR 23.07. Found: C 55.83; 55.60; H 3.70; 3.92; Cl 40.65; 40.80%. C_4H_3Cl . Calculated: C 55.5; H 3.5; Cl 41.0%.

The infrared spectrum, which was determined by Lopatin, contained an absorption band associated with the triple C \equiv C bond ($\nu = 2016\text{ cm}^{-1}$) and one associated with the double C = C bond ($\nu = 1574\text{ cm}^{-1}$); there was a considerable displacement in the position of the C \equiv C absorption band and a very considerable increase in the intensity of the C = C absorption band, which indicates the mutual effects of the bonds.

With ammoniacal cuprous chloride solution the substance gave a brick-red precipitate.

Hexabromide: $CH_2Br-CClBr-CBr_2-CHBr_2$, b.p. 181-182°. Found: C 9.21; 9.19; H 0.38; 0.51, $\Sigma Cl + Br$ 90.77, 90.88. $C_4H_3Br_6Cl$. Calculated: C 8.48; H 0.53; $\Sigma Cl + Br$ 90.80%. Tetrabromide: $C_4H_3Br_4Cl$; b.p. 135-136° (1 mm); n_D^{20} 1.6523. Found: C 12.94; 10.82; H 0.63; 0.55%. $C_4H_3Br_4Cl$. Calculated: C 11.82; H 0.74; $\Sigma Br + Cl$ 87.44%.

By the action of acetone on ethereal 2-chloro-1-buten-3-yne in presence of potassium hydroxide powder we obtained 2,7-dimethyl-3,4-octadiyne-2,7-diol (XIII), m.p. 132°. For (XIII), prepared in a different way, the literature [9] gives m.p. 132-132.5°; 131-132°. Found: C 72.71; 72.55; H 8.60; 8.65%. $C_{10}H_{14}O_2$. Calculated: C 72.25; H 8.5%.

The reaction products remaining after the distillation of butadiyne and 2-chloro-1-buten-3-yne were poured into 1500 ml of water and extracted with ether. We obtained 22.34 g of a fraction of b.p. 50° (5.5 mm), d_4^{20} 1.2525; n_D^{20} 1.4905 as a colorless liquid which readily combined with bromine. Its detailed investigation will be described in a future communication.

Formation of 2-Chloro-4-methoxy-1,3-butadiene (V). A flask fitted with stirrer, reflux condenser, dropping funnel, and thermometer was charged with 122.9 g (1 mole) of 1,4-dichloro-2-butyne and 100 ml of methanol; with stirring at 60° a solution of 115 g of potassium hydroxide in 350 ml of methanol was added over a period of 90 minutes and stirring at the same temperature was continued for one hour. The reaction products were poured into one liter of water and were extracted with ether. The extract was dried over calcium chloride, and ether was distilled off. Vacuum distillation of the low-boiling products in the residue gave 22 g of a fraction with b.p. 37-37.5° (4 mm), a clear colorless liquid which readily combined with bromine with formation of a crystalline bromide; d_4^{20} 1.2157; n_D^{20} 1.4680; Found MR 35.14; Calculated MR 37.87. Found: C 50.80; 50.66; H 6.03; 6.03; Cl 30.10; 30.16%. Calculated C_5H_7OCl : C 50.63; H 5.95; Cl 29.92.

The substance corresponded to 2-chloro-4-methoxy-1,3-butadiene (V).

Dibromide: $CH_3OCHBr-CH=CClCH_2Br$; b.p. 98-100° (4 mm); n_D^{20} 1.5645; d_4^{20} 1.9910; d_4^{20} 1.9875; Found MR 46.51; Calculated MR 46.86. Found: C 20.93; 20.85; H 2.06; 2.01; $\Sigma Cl + Br$ 70.17; 70.10%. $C_5H_7OBr_2$. Calculated: C 21.00; H 2.53; $\Sigma Cl + Br$ 69.97%.

Preparation of 1-Methoxy-1-buten-3-yne (VII). A similar flask was charged with a solution of 120 g of potassium hydroxide in 400 ml of methanol, and 122.9 g of 1,4-dichloro-2-butyne was added at 60-65° over a period of one hour. Stirring was continued at the same temperature for one hour. The reaction products were cooled to room temperature, poured into 1 liter of water, and extracted with ether. Drying with calcium chloride and distillation gave 46.7 g (56.9%) of a fraction of b.p. 50-51° (50.51 mm); a clear mobile liquid with a sharp unpleasant smell; b.p. 40° (40 mm); 50° (50 mm); d_4^{20} 0.9113; n_D^{20} 1.4770; Found MR 25.07; Calculated MR 24.46. Found: C 72.97; 73.08; H 7.73; 7.75%. C_5H_6O . Calculated: C 73.13; H 7.37%.

Our preparation of 1-methoxy-1-buten-3-yne (VII) differed in its constants from that prepared by Herbertz by heating methanol with a technical mixture of 1-buten-3-yne and butadiyne. According to Herbertz [6] 1-methoxy-1-buten-3-yne has: b.p. 63° (80 mm); d_4^{20} 0.91; n_D^{20} 1.462.

When 2 g of 1-methoxy-1-buten-3-yne was heated with 10 ml of 10% sulfuric acid at 60° for 10 minutes we obtained 0.6 g of a crystalline product, which had m.p. 152-163°, corresponding to triacetylbenzene (XV). Found: C 70.28; H 5.92%. $C_{12}H_{12}O_3$. Calculated: C 70.60; H 5.92%.

A mixture with triacetylbenzene melted at 162-163°. For (XV) prepared in another way the literature gives m.p. 162-162.5° [11] and m.p. 163° [12]. By the hydration of 16.41 g (0.2 mole) of 1-methoxy-1-buten-3-yne with a 10% solution of water in methanol in presence of 1 g of mercuric sulfate at 40-45° for two hours we obtained 21.36 g (81%) of acetoacetaldehyde dimethyl acetal (XVI); b.p. 80° (30 mm); d_4^{20} 0.9451; n_D^{20} 1.4150. The literature [11] gives: b.p. 69-70° (20 mm); n_D^{20} 1.4219. Heating of 16.41 g of 1-methoxy-1-buten-3-yne with 50 ml of a 30% solution of potassium hydroxide in methanol in a boiling water bath for eight hours gave 18.0 g (70%) of tetrolaldehyde dimethyl acetal; b.p. 52-54° (12 mm); n_D^{20} 1.4360; d_4^{20} 0.9577; Found MR 31.13; Calculated MR 31.19. Found: C 62.90; 63.19; H 8.62; 8.73%. $C_6H_{10}O_2$. Calculated: C 63.13; H 8.83%.

Preparation of Tetrolaldehyde Dimethyl Acetal (VIII). A solution of 75 g of potassium hydroxide in 200 ml of methanol was added over a period of 30 minutes to 61.5 g (0.5 mole) of 1,4-dichloro-2-butyne at 70-72° with stirring; the mixture was then kept at the same temperature for eight hours. We obtained 40.2 g (70.2%) of tetrolaldehyde dimethyl acetal; b.p. 53-54.5° (12-13.5 mm); n_D^{20} 1.4357.

On hydration of our tetrolaldehyde dimethyl acetal in accordance with Kraft's procedure [13] we obtained acetoacetaldehyde dimethyl acetal; b.p. 75-74° (24-23 mm); n_D^{20} 1.4145.

SUMMARY

1. On reaction of 1,4-dichloro-2-butyne with aqueous-methanolic or methanolic potassium hydroxide the following products may be obtained, depending on the reaction conditions: 2-chloro-1-buten-3-yne, 2-chloro-4-methoxy-1,3-butadiene, butadiyne, 1-methoxy-1-buten-3-yne, and tetrolaldehyde dimethyl acetal.

2. A mechanism is proposed for the acetylene-allene-diene isomerization of 1,4-dichloro-2-butyne in aqueous-alcoholic and alcoholic solutions of potassium hydroxide.

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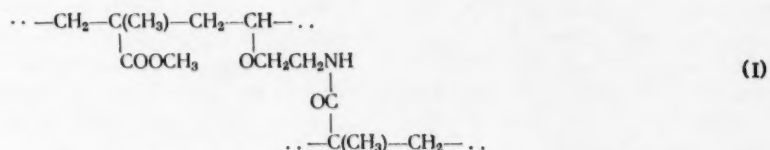
REACTIONS OF UNSATURATED
AND MACROMOLECULAR COMPOUNDS

COMMUNICATION 14. COPOLYMERIZATION OF
GLYCEROL TRIVINYL ETHER WITH METHACRYLIC ACID
AND WITH METHYL METHACRYLATE

M. F. Shostakovskii and A. M. Khomutov

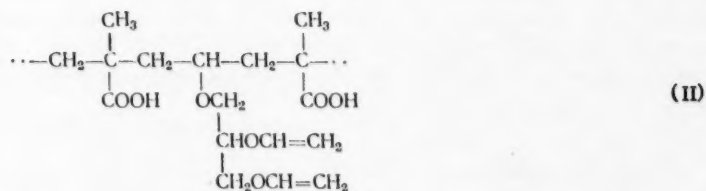
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Among the various kinds of copolymerization which lead to the formation of polymers of three-dimensional structure, there are some new kinds which we have described [1,2] and which are distinguished by the fact that unsaturated compounds containing functional groups are used in the copolymerization reaction. As an example we may cite the copolymer of methyl methacrylate and 2-vinyloxyethylamine:



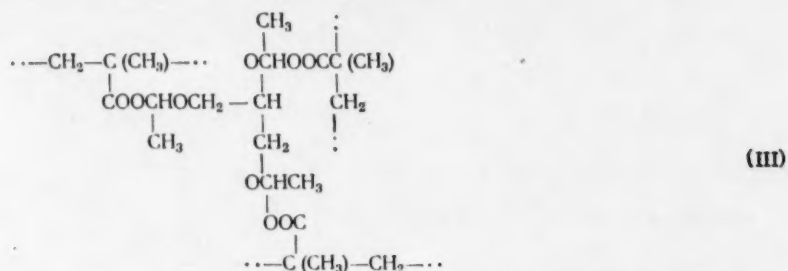
Great interest is presented by the investigation of the copolymerization of vinyl ethers containing two or three vinyl groups in the molecule. For this purpose we took glycerol trivinyl ether [3], and as the second component we used methacrylic acid and also methyl methacrylate. Glycerol trivinyl ether has a large number of reaction centers, and this results in high reactivity. In the copolymerization of glycerol trivinyl ether with methacrylic acid we may expect the following reactions.

a) The formation of copolymers containing free vinyl groups:

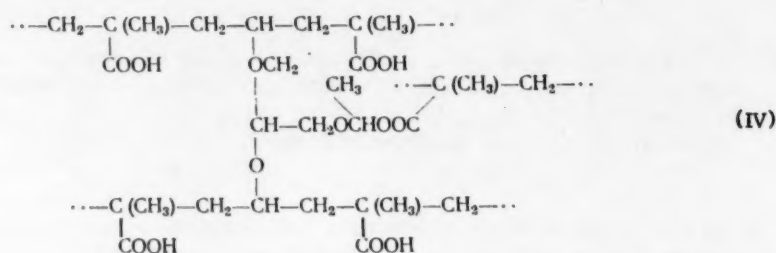


In such a copolymer further internal reactions with the participation of carboxy groups and double bonds, i.e., internal cyclization, are possible.

b) The formation of branched copolymers of the following structure:



c) Finally there may be reaction in which three-dimensional copolymers are formed which are insoluble in organic solvents:



The cross-linking of the molecules in the copolymer occurs only when the original monomers are taken in equimolecular proportions, in which case two copolymers are isolated. One is of three-dimensional structure, for it is insoluble and infusible. The formation of a three-dimensional copolymer could occur as a result of the simultaneous participation of the vinyl groups of glycerol trivinyl ether in the copolymerization and as a result of the formation of acylals (IV). The structure of this three-dimensional copolymer was proved by hydrolysis. We then isolated acetaldehyde, but the residual copolymer was insoluble and infusible. At the same time we obtained ether-soluble copolymers. On their hydrolysis we isolated acetaldehyde. The structure of this copolymer probably corresponded to Scheme (III).

It follows that the copolymerization of glycerol trivinyl ether with methacrylic acid proceeds in several directions with formation of a complex mixture of copolymers. However, in this reaction we may observe several regularities which coincide with those previously established for other vinyl ethers [4, 5]. Increase in the amount of glycerol trivinyl ether in the reaction mixture lowers the yields of copolymers and raises the content of units of this vinyl ether in the copolymer chain.

We studied also the copolymerization of glycerol trivinyl ether with methyl methacrylate. The latter does not contain an active functional group capable of reacting with the double bonds of glycerol trivinyl ether. The copolymerization of these compounds was carried out with the aim of determining the possibility of forming cross-linked three-dimensional copolymers. Our study showed that in this case copolymerization was not accompanied by cross-linking of the molecules. The copolymers obtained were readily soluble in acetone.

EXPERIMENTAL

The monomers were freshly distilled for use and had the following properties: Methyl methacrylate: b.p. 100.5°; n_D^{20} 1.4150; d_4^{20} 0.9361. Methacrylic acid: b.p. 160° n_D^{20} 1.4313; d_4^{20} 1.0153; acid value 650 mg of KOH. Glycerol trivinyl ether: b.p. 164-165°; n_D^{20} 1.4381; d_4^{20} 1.0335. The conditions and experimental procedure in the copolymerization are described in the literature [1].

Copolymerization of Glycerol Trivinyl Ether with Methacrylic Acid. For the copolymerization we took 1.68 g of methacrylic acid and 3.32 g of glycerol trivinyl ether (molar ratio 1:1). We obtained two copolymers.

TABLE 1

Yields and Compositions of Copolymers of Methacrylic Acid (I)
and Glycerol Trivinyl Ether (II)

Molar composition of monomer mixture (%)		Yield of polymer or copolymer (%)	Carboxyl content of polymer or copolymer (% by wt)	Molar composition (%) in copolymer of residues of	
I	II			I	II
100	—	91,5	99,8	100	—
95	5	84,6	99,0	99,5	0,5
75	25	60,6	81,95	90,0	10,0
50	50	53,2	77,50*	87,1	12,9
			54,0	70,0	30,0
25	75	21,8	64,76	78,4	21,6
5	95	Does not polymerize			
—	100	»			

*Two copolymers of different composition and structure were isolated.

TABLE 2

Yields of Copolymers of Methyl Methacrylate (I)
and Glycerol Trivinyl Ether (II)

Molar composition of monomer mixture (%)		Yield of polymer or copolymer (%)	Acetal groups found in copolymer (%)	Acetal groups found in by-products (%)
I	II			
100	—	94,5	—	—
75	25	67,2	—	4,48
50	50	43,6	6,0	20,0
25	75	12,4	—	—
—	100	Does not polymerize		

One was infusible and was insoluble in water, methanol, acetone, dioxane, diethyl ether, benzene, chloroform, and other solvents. In methanol, for example, the copolymer gave a swollen gel. To remove unchanged monomers, the swollen copolymer was treated with diethyl ether until a test for a double bond was negative. As the carbon contents of the monomers were very close in value (methacrylic acid 55,8% C, glycerol trivinyl ether, 60,35% C), no purpose was served by carrying out elementary analysis.

The compositions of the copolymers were established by the determination of carboxy groups. After the hydrolysis of the copolymer we found acetaldehyde, and we calculated the content of glycerol trivinyl ether residues and obtained values of 13,28% and 12,9%.

After the separation of the copolymers in methanol-ether solution we determined unchanged monomers and other reaction products. The methanol-ether solution was evaporated in a vacuum. There remained 2,16 g of liquid in the flask, and in this we determined methacrylic acid and acetaldehyde. We could not distill this liquid because it decomposed and turned yellow when heated. The copolymerization of the same monomers was studied at other molar ratios. At the end of the reaction the products were treated under the conditions in the experiment described (Table 1).

Copolymerization of Glycerol Trivinyl Ether with Methyl Methacrylate. For the copolymerization we took 1,85 g of methyl methacrylate and 3,15 g of glycerol trivinyl ether (molar ratio 1:1). The conditions of copolymerization and purification are given above. The copolymer was readily soluble in acetone and was precipitated by methanol. Bromine water was added to a solution of the copolymer: the solution was not decolorized, which indicated the absence of double bonds. As both of the monomers contained about 60% of carbon, no purpose was served by carrying out elementary analysis. We did not succeed in effecting the quantitative hydrolysis of ester groups of methyl methacrylate residues in the copolymer. The copolymer was hydrolyzed, and the acetaldehyde formed was determined. The last determination was carried out by the usual method: the copolymer was hydrolyzed by heating it with acid, and acetaldehyde was determined by the sulfite method. After the separation of the copolymers, methyl methacrylate, glycerol trivinyl ether, and the residue after vacuum distillation of solvents were determined in the solution. Acetaldehyde was determined in the solution by the sulfite method. Distillation of solvents left a residue of 1,79 g, in which we determined acetaldehyde after hydrolysis. We could not resolve the components of this residue; it probably consisted of a mixture of substances formed as a result of the

transformations of the original monomers. We studied also the copolymerization of the same monomers at different molar ratios. At the end of the reaction the products were treated under the conditions of the preceding experiments. The yields and results of the investigations are given in Table 2.

SUMMARY

1. The copolymerization of glycerol trivinyl ether with methacrylic acid and with methyl methacrylate were investigated. Some new copolymers were synthesized.

2. In the preparation of copolymers of methyl methacrylate and glycerol trivinyl ether the formation of three-dimensional copolymers was not observed.

3. Three-dimensional copolymers of glycerol trivinyl ether and methacrylic acid are obtained only when the monomers are taken in equimolecular proportions.

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CONDITIONS FOR THE ISOMERIZATION OF α -ALKYL(OR ARYL)FURFURYL ALCOHOLS

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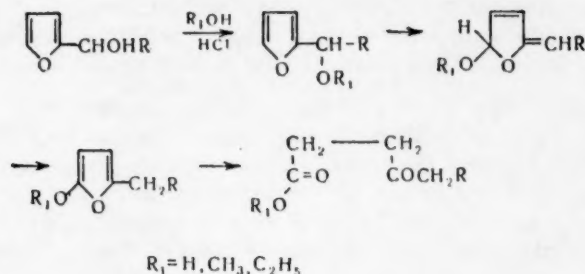
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The cleavage of the furan ring under the action of mineral acids was discovered in 1887 by Dietrich and Paal [1] for the case of 2-methylfuran. This reaction was later studied by various investigators [2], who showed that many furan compounds can undergo this sort of change. In 1932 Chichibabin [3], who carried out the isomerization of α -alkylfurfuryl alcohols, proposed a mechanism for this reaction. However, a more detailed study of the mechanism was carried out in 1944 by Ushakov and Kucherov [4]. Having isolated and established the structures of the intermediate products in the isomerization, they showed that the transformations of α -alkyl(or aryl)furfuryl alcohols into γ -keto acids have ionotropic mechanisms associated with the migration of double bonds.



This interpretation of the mechanism later found confirmation in the work of Lewis and others [5].

As we have reported previously [6], for the synthesis of sulfur-containing heterocyclic compounds we prepared a series of α -alkyl(aryl)furfuryl alcohols from organomagnesium compounds and 2-furaldehyde, and we carried out their isomerization into the ethyl esters of the corresponding γ -keto acids. In view of the relatively limited data in the literature on the isomerization of α -alkylfurfuryl alcohols, we turned particular attention on the choice of optimum conditions, under which the yields of isomerization products would attain maximum values. In the isomerization of α -alkylfurfuryl alcohols of low molecular weight, Ushakov and Kucherov [4] used 0.35-0.5% of hydrogen chloride in alcohol. This concentration was found to be quite inadequate for the isomerization of alcohols of high molecular weight. Thus, in the isomerization of α -7-methylheptylfurfuryl alcohol with 0.3% alcoholic hydrogen chloride the yield of ethyl 6-methyl-4-oxododecanoate was only 5.5%. If, however, the concentration of HCl was raised to 8.5%, the yield of product was increased to 50%. Chichibabin [3] also used a low concentration of hydrogen chloride, irrespective of the structure of the original alcohol. We found that the concentration of hydrogen chloride and the time for which the reaction mixture is boiled have to be varied according to the molecular weight and structure of the α -alkylfurfuryl alcohol taken.

Original furfuryl alcohol	HCl concn. (%)	Time of boiling (hr)	Yield of γ -keto ester (%)	Original furfuryl alcohol	HCl concn. (%)	Time of boiling (hr)	Yield of γ -keto ester (%)
α -Methylfurfuryl alcohol	0,2	3	38	α -Isopentylfurfuryl alcohol	0,39	3	44
α -Ethylfurfuryl alcohol	0,35	3	48	α -t-Pentylfurfuryl alcohol	0,2	3	6,6
α -Propylfurfuryl alcohol	0,38	3	46,7	α -Heptylfurfuryl alcohol	3,7	0,5	34,7
α -Isopropylfurfuryl alcohol	0,36	3	52	α -Octylfurfuryl alcohol	3,2	0,5	49,6
α -Butylfurfuryl alcohol	0,35	3	49	α -(1-Methylheptyl)furfuryl alcohol	5,3	0,5	47,5
α -s-Butylfurfuryl alcohol	0,35	3	64	α -Decylfurfuryl alcohol	0,35	3	5,5
α -Isobutylfurfuryl alcohol	0,3	3	46		8,5	0,5	50,0
	2,0	0,5	52		6,3	0,5	30
α -t-Butylfurfuryl alcohol	0,5	3	21		9,0	0,5	59,6
	4,0	0,5	38	α -Benzylfurfuryl alcohol	12,7	0,5	46
α -Pentylfurfuryl alcohol	0,5	3	38,5		0,4	3	17*
	4,2	0,5	48		4,0	0,5	tar
				α -Phenethylfurfuryl alcohol	0,35	3	47

*As acid.

It is known that all α -alkylfurfuryl alcohols are extremely acidophobic, but they nevertheless differ amongst themselves in stability toward acids. Thus, α -alkylfurfuryl alcohols of low molecular weight and those containing a tertiary carbon atom in the side chain are strongly resinified in an alcoholic solution of hydrogen chloride, and the yields of isomerization products did not exceed 30-40% in spite of the fact that we used very varied reaction conditions. For the isomerization of alcohols of high molecular weight and normal structure an increased concentration of hydrogen chloride was required: when the concentration of hydrogen chloride was low, part of the starting substance was recovered unchanged. Thus, we found that in the isomerization of α -decylfurfuryl alcohol in alcoholic solution containing 9.5% of HCl the yield of ethyl 4-oxopentadecanoate attained 60%. If, however, the concentration of hydrogen chloride was reduced to 6%, the yield of isomerization product was lowered to 30%. An excessively high concentration (13%) also lowers the yield (to 46%) because of increased resin formation.

A peculiar isomerization picture was found in the case of the three furfuryl alcohols containing an aromatic group in the side chain. It was found that, as the phenyl group approaches the hydroxy group in the alcohol, the yield of isomerization products diminishes. Thus, we could not obtain an appreciable amount of the keto ester in the isomerization of α -phenylfurfuryl alcohol. Even when the minimum concentration of hydrogen chloride was used, there was almost complete resinification of the product. α -Benzylfurfuryl alcohol is capable of isomerization with formation of ethyl 4-oxo-6-phenylhexanoate, though in low yield (20% of the acid), but we did not succeed in obtaining it in a pure state because of contamination with bibenzyl (present in original alcohol) and with a neutral product of unestablished structure formed in the isomerization. Unlike these two alcohols, α -phenethylfurfuryl alcohol, according to our own results and those of Kucherov [7], can be isomerized in yields of up to 48%, like an ordinary α -alkylfurfuryl alcohol.

The effect of the concentration of hydrogen chloride and the duration of the boiling on the yield of γ -keto ester obtained in the isomerization of α -alkylfurfuryl alcohols can be seen from the table.

EXPERIMENTAL

Preparation of Some α -Alkylfurfuryl Alcohols

α -s-Butylfurfuryl Alcohol. A solution of 260 g of 2-furaldehyde in 300 ml of dry ether was added dropwise at -10° to a constantly stirred Grignard reagent prepared from 94 g of magnesium and 460 g of 2-bromobutane in 1200 ml of dry ether. The reaction mixture was then stirred with cooling for 40 minutes, after which it was boiled for 1.5-2 hours. The resulting magnesium complex was poured onto a large amount of ice, the ether layer that separated was decanted, and the mass of benzylfurfuryl alcohol that remained was carefully extracted with ether. The combined ether extract was washed with saturated potassium carbonate solution, then with 40% sodium

bisulfite solution, and finally it was dried with fused potassium carbonate. Solvent was distilled off, and the residue was vacuum-distilled twice through a column. This gave 292 g (70% on the 2-furaldehyde taken) of α -s-butylfurfuryl alcohol; b.p. 80-82° (4 mm); n_D^{20} 1.4739; d_4^{20} 0.9917; Found MR 43.70; Calculated MR 43.79.

α -Pentylfurfuryl Alcohol. In a similar way, from 605 g of pentyl bromide, 145 g of magnesium, and 335 g of 2-furaldehyde in 2000 ml of dry ether we obtained 498 g (85%) of the alcohol; b.p. 99-101° (3 mm); n_D^{20} 1.4695; d_4^{20} 0.9772; Found MR 48.03; Calculated MR 48.41. Found: C 71.41; 71.24; H 9.50; 9.37%. $C_{10}H_{16}O_2$. Calculated: C 71.39; H 9.53%.

α -Isopentylfurfuryl Alcohol [8]. This was prepared similarly from 527 g of isopentyl bromide, 105 g of magnesium, and 297 g of 2-furaldehyde in 1600 ml of dry ether in 85% yield; b.p. 94-94.5° (4 mm); n_D^{20} 1.4695; d_4^{20} 0.9745; Found MR 48.41; Calculated MR 48.41.

α -t-Pentylfurfuryl Alcohol. This was prepared similarly from 176 g of t-pentyl chloride, 60 g of magnesium, and 120 g of 2-furaldehyde in 1200 ml of dry ether in 69% yield. In view of the instability of the resulting furfuryl alcohol, it was not distilled. It was a slightly colored viscous liquid, n_D^{20} 1.4808.

α -Heptylfurfuryl Alcohol. This was prepared in 88.3% yield from 564 g of heptyl bromide, 110 g of magnesium, and 249 g of 2-furaldehyde in 2200 ml of dry ether by a procedure similar to those given above, but with the difference that the Grignard reagent was prepared with external heating. The furfuryl alcohol obtained by vacuum distillation through a column had: b.p. 105-106° (2 mm); n_D^{20} 1.4686; d_4^{20} 0.9524; Found MR 57.35; Calculated MR 57.64. Found: C 73.50; 73.31; H 10.47; 10.33%. $C_{12}H_{20}O_2$. Calculated: C 73.43; H 10.27%.

α -Octylfurfuryl Alcohol. In a similar way, from 314 g of octyl bromide, 64 g of magnesium, and 116.4 g of 2-furaldehyde in 1600 ml of dry ether we obtained 225 g (95.5%) of α -octylfurfuryl alcohol; b.p. 114-115° (3 mm); n_D^{20} 1.4670; d_4^{20} 0.9351; Found MR 62.40; Calculated MR 62.25. Found: C 74.39; H 10.40%. $C_{13}H_{22}O_2$. Calculated: C 74.24; H 10.54%.

α -(1-Methylheptyl)furfuryl Alcohol. This was prepared in a similar way from 300 g of 2-bromooctane, 44 g of magnesium, and 140 g of 2-furaldehyde in 750 ml of dry ether in 75% yield. In view of its instability to heat, the product was not distilled. Light fractions were vacuum-distilled off, and the product was then found to be a yellowish liquid; n_D^{20} 1.4660; d_4^{20} 0.9233; Found MR 63.08; Calculated MR 62.27.

α -Decylfurfuryl Alcohol. This was prepared similarly from 160 g of decyl bromide, 21 g of magnesium, and 60 g of 2-furaldehyde in 230 ml of dry ether in 82% yield. After vacuum distillation [b.p. 139-142° (2 mm)] the product solidified; m.p. 32-33°. Found: C 75.20; H 10.92%. $C_{15}H_{26}O_2$. Calculated: C 75.59; H 10.96%.

α -Benzylfurfuryl Alcohol [9]. This was prepared similarly from 260 g of benzyl chloride, 60 g of magnesium, and 175 g of 2-furaldehyde in 820 ml of dry ether in 31.5% yield. The product was a yellowish viscous liquid; b.p. 115-117° (2 mm); n_D^{20} 1.5559; d_4^{20} 1.1279; Found MR 53.65; Calculated MR 54.65. The low yield of the benzylfurfuryl alcohol is to be explained first by the formation of bibenzyl (10 g, m.p. 51-53°) as a by-product in the Grignard synthesis, and second by the instability of the benzylfurfuryl alcohol to heat [10]. The refractive index of the benzylfurfuryl alcohol varied over a fairly wide range: n_D^{20} 1.5549-1.5609.

α -Phenethylfurfuryl Alcohol [11]. This was prepared similarly from 620 g of phenethyl bromide, 82 g of magnesium, and 248 g of 2-furaldehyde in 1650 ml of dry ether in 92% yield (480 g); b.p. 149-152° (3.5 mm); n_D^{20} 1.5548.

Preparation of γ -Keto Esters

Ethyl 4-Oxohexanoate [3, 4]. A solution of 215 g of α -methylfurfuryl alcohol [12] [b.p. 76-77° (23 mm); n_D^{20} 1.4793] in 820 ml of 0.2% alcoholic hydrogen chloride was boiled for three hours in a water bath, after which the solution was distilled down to one-third bulk and the residue was poured into a saturated solution of potassium carbonate. The product was extracted with ether, and the ether extracts were dried over fused potassium carbonate. Solvent was distilled off, and two vacuum distillations of the residue through a 50-cm column gave 116.5 g (38%) of ethyl 4-oxohexanoate, b.p. 76-77° (3 mm) and n_D^{20} 1.4330, which corresponds to data in the literature.

Ethyl 4-Oxoheptanoate [3]. This was prepared similarly from 317 g of α -ethylfurfuryl alcohol [12, 13] [b.p. 70-72° (8 mm); n_D^{20} 1.4744] in 1160 ml of 0.35% alcoholic hydrogen chloride in 48% yield; b.p. 96-98° (4 mm); n_D^{20} 1.4312; d_4^{20} 0.9780; Found MR 45.60; Calculated MR 45.43.

Ethyl 4-Oxo-octanoate. In a similar way, by boiling 279 g of α -propylfurfuryl alcohol [12] [b.p. 103-104° (25 mm); n_D^{20} 1.4770] in 850 ml of 0.38% alcoholic hydrogen chloride for three hours we obtained 173 g (46.7%) of ethyl 4-oxo-octanoate; b.p. 93-94° (2.5 mm); n_D^{20} 1.4340; d_4^{20} 0.9640; Found MR 50.31; Calculated MR 50.05.

Ethyl 6-Methyl-4-oxoheptanoate [4]. Similarly, from 235 g of α -isopropylfurfuryl alcohol [12] [b.p. 74-75° (11 mm); n_D^{20} 1.4725] in 850 ml of 0.35% alcoholic hydrogen chloride we obtained 159 g (52%) of ethyl 6-methyl-4-oxoheptanoate; b.p. 80-81° (3 mm); n_D^{20} 1.4293; d_4^{20} 0.9585; Found MR 50.11; Calculated MR 49.93; Calculated 52%.

Ethyl 4-Oxononanoate [7]. From 336 g of α -butylfurfuryl alcohol [12, 13] [b.p. 98-100° (5 mm); n_D^{18} 1.4728] in 1200 ml of 0.35% alcoholic hydrogen chloride we obtained 213 g (49%) of the keto ester, b.p. 111-113° (5 mm) and n_D^{20} 1.4367, which corresponds to data in the literature.

Ethyl 6-Methyl-4-oxooctanoate. In a similar way, by boiling 292 g of α -s-butylfurfuryl alcohol in 1100 ml of 0.35% alcoholic hydrogen chloride for three hours we obtained 250 g (64%) of the corresponding γ -keto ester; b.p. 110-111° (4 mm); n_D^{20} 1.4342; d_4^{20} 0.9546; Found MR 54.61; Calculated MR 54.66. Found: C 65.87; 65.64; H 10.18; 10.40%. $C_{11}H_{20}O_3$. Calculated: C 65.96; H 10.06%.

Ethyl 7-Methyl-4-oxooctanoate [7]. This was prepared similarly from 425 g of α -isobutylfurfuryl alcohol [12] [b.p. 79-80° (4 mm); n_D^{20} 1.4685] in 1500 ml of 2% alcoholic hydrogen chloride in 52% yield; b.p. 90-91° (3 mm) and n_D^{20} 1.4330, which corresponds to data in the literature.

Ethyl 6,6-Dimethyl-4-oxoheptanoate [4]. A solution of 179 g of α -t-butylfurfuryl alcohol [4] (because of its instability to heat the alcohol was not distilled; n_D^{20} 1.4807) in 570 ml of 4% alcoholic hydrogen chloride was boiled for 30 minutes. The usual treatment and two distillations gave ethyl 6,6-dimethyl-4-oxoheptanoate in 38% yield; b.p. 88-89° (3.5 mm); n_D^{20} 1.4346; d_4^{20} 0.9523; Found MR 54.83; Calculated MR 54.66.

Ethyl 4-Oxodecanoate. α -Pentylfurfuryl alcohol (190 g) was dissolved in 450 g of absolute alcohol and saturated with 20 g (determined by increase in weight) of dry hydrogen chloride. The reaction mixture was then boiled for 30 minutes and treated as described above. Two distillations gave 116 g (48%) of the γ -keto ester; b.p. 115-116° (3 mm); n_D^{20} 1.4370; d_4^{20} 0.9440; Found MR 59.55; Calculated MR 59.28. Found: C 67.34; 67.23; H 10.30; 10.45%. $C_{12}H_{22}O_3$. Calculated: C 67.26; H 10.35%.

Ethyl 8-Methyl-4-oxononanoate. By boiling 250 g of α -isopentylfurfuryl alcohol in 900 ml of 0.39% alcoholic hydrogen chloride for three hours we obtained 140 g (44%) of ethyl 8-methyl-4-oxononanoate; b.p. 112-114° (3 mm); n_D^{20} 1.4373; d_4^{20} 0.9432; Found MR 59.55; Calculated MR 59.28. Found: C 67.67; 67.65; H 10.37; 10.58%. $C_{12}H_{22}O_3$. Calculated: C 67.26; H 10.35%.

Ethyl 6,6-Dimethyl-4-oxooctanoate. By boiling 145 g of α -t-pentylfurfuryl alcohol in 300 ml of 3.7% alcoholic hydrogen chloride for 30 minutes and suitable treatment we obtained 64 g (34.7%) of the γ -keto ester; b.p. 95-97° (2 mm); n_D^{20} 1.4410; d_4^{20} 0.9562; Found MR 59.19; Calculated MR 59.28. Found: C 67.44; H 10.35%. $C_{12}H_{22}O_3$. Calculated: C 67.29; H 10.35%.

Ethyl 4-Oxododecanoate. In a similar way, from 316 g of α -heptylfurfuryl alcohol in 700 ml of 3.2% alcoholic hydrogen chloride we obtained 194 g (49.6%) of the keto ester; b.p. 131-133° (2 mm); n_D^{20} 1.4403; d_4^{20} 0.9317; Found MR 68.59; Calculated MR 68.52. Found: C 69.47; 69.72; H 10.93; 10.94%. $C_{14}H_{26}O_3$. Calculated: C 69.38; H 10.83%.

Ethyl 4-Oxotridecanoate. This was prepared similarly from 126 g of α -octylfurfuryl alcohol in 400 ml of 5.3% alcoholic hydrogen chloride in 47.5% yield (73 g); b.p. 145-146° (3 mm); n_D^{20} 1.4430; d_4^{20} 0.9256; Found MR 73.43; Calculated MR 73.14. Found: C 70.49; 70.69; H 11.24; 11.16%. $C_{15}H_{28}O_3$. Calculated: C 70.29; H 11.01%.

Ethyl 6-Methyl-4-oxododecanoate. Similarly, by boiling 200 g of α -(1-methylheptyl)furfuryl alcohol in 600 ml of 8.5% alcoholic hydrogen chloride for 30 minutes we obtained 122 g (50%) of the keto ester; b.p. 123-125° (1 mm). n_D^{20} 1.4411; d_4^{20} 0.9232; Found MR 73.23; Calculated MR 73.135. Found: C 69.98; 69.99; H 10.95; 10.90%. $C_{15}H_{28}O_3$. Calculated: C 70.29; H 11.01%.

Ethyl 4-Oxopentadecanoate. Similarly, from 50 g of α -decylfurfuryl alcohol in 120 ml of 9.5% alcoholic hydrogen chloride we obtained the keto ester in 59.6% yield. Ethyl 4-oxopentadecanoate is a white crystalline substance, m.p. 25-27° (it crystallizes after two distillations); b.p. 166-167° (2.5 mm). Found: C 72.15; 71.94; H 11.52; 11.58%. $C_{17}H_{32}O_3$. Calculated: C 71.78; H 11.34%.

4-Oxo-6-phenylhexanoic Acid. A solution of 59 g of α -benzylfurfuryl alcohol in 200 ml of 0.4% alcoholic hydrogen chloride was boiled for three hours in a water bath. After the usual treatment and two distillations we obtained 38.4 g of product, b.p. 127-129° (1.5 mm), n_D^{20} 1.4898; d_4^{20} 1.0311, which was hydrolyzed at the boil for two hours with a solution of 27 g of potassium hydroxide in 250 ml of methanol. The residue remaining after removal of solvent was poured into water, and the upper layer of unhydrolyzed material was extracted with ether; the extract was dried with potassium carbonate and vacuum-distilled: b.p. 140-141 (1 mm); n_D^{20} 1.4826; d_4^{20} 1.0194. Found: C 71.09; 71.13. H 9.22. 9.40%.

The aqueous solution was acidified with concentrated hydrochloric acid, and the yellow precipitate formed was filtered off and crystallized from hot water. We obtained 6 g of 4-oxo-6-phenylhexanoic acid, m.p. 93-94°. Found: C 69.69. 69.73; H 6.72; 6.42%. $C_{12}H_{14}O_3$. Calculated: C 69.92; H 6.72%.

Ethyl 4-Oxo-7-phenylheptanoate [7]. Similarly, by boiling 280 g of α -phenethylfurfuryl alcohol in 1000 ml of 0.35% alcoholic hydrogen chloride for three hours we obtained 162 g (47%) of the keto ester, b.p. 166-169° (3 mm) and n_D^{20} 1.5010, which corresponds to data in the literature.

SUMMARY

1. A study was made of the conditions required for the isomerization of some α -alkyl(and aryl)furfuryl alcohols in an alcoholic solution of hydrogen chloride.
2. The yield of isomerization product depends considerably on the structure of the α -alkylfurfuryl alcohol and also on the concentration of hydrogen chloride.
3. Seventeen α -alkyl(and aryl)furfuryl alcohols and seventeen ethyl esters of γ -keto acids, most of which have not been described previously, were prepared and characterized.

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CATALYTIC POLYMERIZATION OF OLEFINS

COMMUNICATION 10. EFFECT OF TEMPERATURE

AND TIME OF CONTACT ON THE COURSE OF

THE POLYMERIZATION OF ETHYLENE

OVER NICKEL CATALYSTS

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In the present work we investigated the effect of various factors on the course of the polymerization of ethylene over nickel catalysts that we have described previously [1]; the factors investigated were: temperature, time of contact, and length of catalyst layer. The apparatus and experimental procedure were as before [2]. The duration of each experiment was 5-6 hours.

TABLE 1

Expt.	Reaction temp. (°C)	Amt. of ethylene that reacted	Yield of butene (%)		Yield of higher hydrocarbons (%)	
			on ethylene passed	on ethylene that reacted	on ethylene passed	on ethylene that reacted
1-2	200	42,8-13,2	21,8-0,5	51,6-3,6	2,7-2,1	5,1-16,1
3*	100	19,4	1,1	5,6	0,0	0,0
4*-5	100-150	25,3-17,2	0,6-0,0	2,4-0,0	0,0-0,0	0,0-0,0
6-7	200-250	19,6-19,1	0,0-0,0	0,0-0,0	0,0-0,0	0,0-0,0
8-9	250-300	28,6-1,4	8,8-1,4	30,7-5,7	1,5-0,0	5,4-0,0
10*-11	300	39,6-12,7	11,6-2,5	29,4-20,0	2,9-0,3	7,5-2,9

*Before this experiment the catalyst was regenerated in a stream of air at 440° for four hours.

EXPERIMENTAL

Effect of Reaction Temperature. Results on the work of the formate-impregnation NiO-aluminum silicate catalyst in tablet form designated as Catalyst 124 [3] are presented in Table 1. The length of the catalyst layer was 16 cm. Experiments on the polymerization of ethylene were carried out at 100°, 150°, 200°, 250°, and 300° for a time of contact of 12 seconds. Over this catalyst at 200° the conversion of ethylene was 43% in the first five hours of work; the yield of butene was 21.8% on the amount of ethylene passed and 51.6% on the amount that reacted. However, in the next five hours the conversion fell to 13.2% and the yield of butene was extremely

TABLE 2

Expt.	Reaction temp(°C)	Time of contact (sec)	Amt. of ethylene that reacted	Yield of butene (%)		Yield of higher hydrocarbons (%)	
				on ethylene passed	on ethylene that reacted	on ethylene passed	on ethylene that reacted
1	200	17,0	0,0	0,0	0,0	0,0	0,0
2	215	15,5	0,0	0,0	0,0	0,0	0,0
3	230	15,2	0,0	0,0	0,0	0,0	0,0
4	250	15,8	0,0	0,0	0,0	0,0	0,0
5	300	6,0	30,0	18,3	62,0	5,2	17,7
6*	250	6,4	35,0	22,1	63,2	6,0	17,0
7*	225	8,2	28,0	15,6	68,0	3,0	13,5
8*	225	7,3	11,3	7,3	64,3	1,8	16,0

*Before this experiment the catalyst was regenerated in a stream of air at 450° for five hours.

TABLE 3

Expt.	Reaction temp.(°C)	Amt. of ethylene that reacted	Yield of butene (%)		Yield of higher hydrocarbons (%)	
			on ethylene passed	on ethylene that reacted	on ethylene passed	on ethylene that reacted
1	200	0,0	0,0	0,0	0,0	0,0
2	225	10,4	6,4	61,5	2,1	20,0
3	250	12,6	7,5	60,0	2,1	16,8
4	250	7,1	3,4	48,0	1,6	22,2
5	250	21,7	14,5	68,1	5,3	25,0
6	250	14,3	9,5	66,6	3,2	22,1
7	275	26,6	15,3	57,6	5,3	21,1
8	275	20,5	10,9	53,3	4,5	22,1
9	300	35,0	20,0	57,1	8,7	24,8

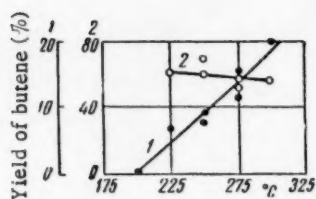


Fig. 1. Temperature-dependence of rate of polymerization of ethylene: 1) yield of butene (% on ethylene passed); 2) yield of butene (% on ethylene that reacted).

dimer, on the ethylene passed and the ethylene that reacted, were 18.3% and 62%, respectively. The productivity of the catalyst was 133 g/liter·hr. After regeneration and lowering of the temperature to 250° the activity and selectivity of the catalyst remained the same. After regeneration and lowering of the temperature to 225° the conversion fell to 23% and the yields of dimer to 15.6% and 68.0%, respectively. Comparison of the results of Experiments 4 and 6 (Table 2) shows that in this case also, with a preliminary passage of ethylene over the catalyst at relatively lower temperatures, reaction does not go, and the catalyst is poisoned.

low. After regeneration in a stream of air at 440°, the catalyst was of extremely low activity at 100°; after a second regeneration the catalyst showed no activity at 100-200°, but at 250-300° the polymerization of ethylene went to a small extent. After a new regeneration the conversion was already almost 40% with a yield of butene of 11.6% on the ethylene passed. The catalyst then showed low selectivity with respect to dimerization. Comparison of Experiments 9 and 10 shows that with a preliminary passage of ethylene over the catalyst at a lower temperature reaction does not go, and the catalyst is poisoned.

Table 2 gives the results of experiments with Catalyst 234, which was obtained by precipitation with ammonia from nickel nitrate and was an NiO - aluminum silicate (finely spherical) catalyst [4]; the length of the layer was 7 cm. Table 2 shows that at 200-250° with a time of contact of 6 seconds the conversion of ethylene was 30% and the yields of

TABLE 4

Catalyst	Time of contact (sec)	Reaction temp. (°C)	Yield of butene (%)		Yield of higher hydrocarbons (%)	
			on ethylene passed	on ethylene that reacted	on ethylene passed	on ethylene that reacted
241	4,9	13,0	7,4	56,5	3,0	24,2
243	7,0	50,2	28,5	56,8	10,7	21,3
252	3,5	12,5	9,8	78,9	3,2	26,3
237	5,5	36,2	21,1	58,3	7,9	21,8

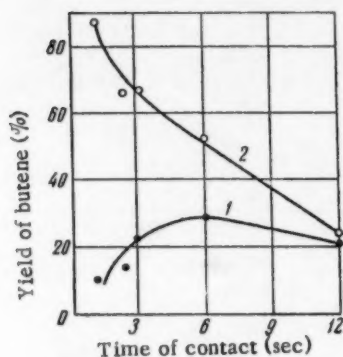


Fig. 2. Effect of time of contact on the course of the polymerization of ethylene over an impregnation catalyst: 1) yield of butene (% on ethylene passed); 2) yield of butene (% on ethylene that reacted).

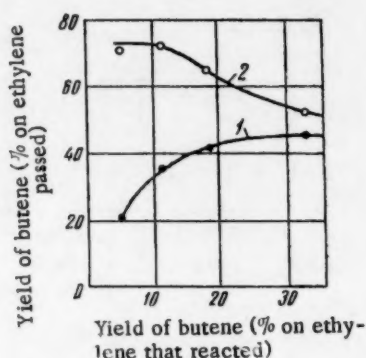


Fig. 3. Effect of time of contact on the course of the polymerization of ethylene over a precipitation catalyst: 1) yield of butene (% on ethylene passed); 2) yield of butene (% on ethylene that reacted).

In Table 3 and Fig. 1 we present the results on the work of Catalyst 238, which was a mixture of finely ground finely spherical aluminum silicate with nickel silicate, similar in preparation and composition to Catalyst 237, described in the preceding communication [5]; length of layer 6 cm. The catalyst was activated in a stream of air at 300° for one hour and was regenerated after each experiment in a stream of air at 450° for five hours. The time of contact was 7-8 seconds. At 200° Catalyst 238 was inactive, and at 225° the activity was low. A somewhat higher activity was observed at 250°, and the optimum temperature range was 175-300°.

Effect of Time of Contact on Reaction. We studied the effect of the time of contact on the course of the polymerization of ethylene. Table 4 gives results for the first five hours of work of Catalysts 243, 237, and 252, which have been described previously [5], and of Catalyst 241. All these catalysts were prepared from a finely dispersed mixture of nickel silicate and aluminum silicate (finely spherical). In these experiments, which were carried out at 300°, comparisons should be made of the results obtained with Catalysts 241 and 243, which had the same composition, and also of the results obtained with Catalysts 252 and 237, which also had identical compositions. In these experiments the space velocity was varied by varying the linear velocity. The diameter of the tube and the volume of the catalyst were not altered. The latter was 5 ml.

In Table 5 and Fig. 2 we present results on the work of a formate-impregnation catalyst, the carrier for which was an aluminum silicate "treating" catalyst in tablet form [3]. The space velocity was changed by using 1, 1/2, 1/4, etc., of a portion of catalyst, i.e., by changing the volume of the catalyst. The experiments were carried out at 300° (Catalysts 100, 130, 141) and 250° (Catalysts 131, 137).

TABLE 5

Catalyst	Number of		Volume of catalyst, ml	Time of contact (sec)	Reaction temp. (°C)	Amt. of ethylene that reacted	Yield of butene (%)		Yield of higher hydrocarbons (%)	
	Expt.						on ethylene passed	on ethylene that reacted	on ethylene passed	on ethylene that reacted
400	1-2		10	12	300	89.0-57.5	24.6-36.7	24.2-63.9	35.2-43.0	39.5-22.6
430	1-2		5	6	300	56.0-32.9	30.4-20.2	52.4-60.8	3.0-2.9	5.1-8.8
441	1-2		2.5	3	300	34.5-19.9	23.0-13.0	67.0-69.5	6.0-2.7	17.2-13.8
431	1-2		2.5	2.5	250	48.8-10.1	12.6-12.3	63.2-81.2	2.4-2.8	12.1-18.6
437	1-2		1.0	1.2	250	11.1-2.4	9.8-4.3	88.7-23.3	2.2-1.7	19.6-9.2

TABLE 6

Catalyst	Number of		Vol. of catalyst (ml)	Time of contact (sec)	Amt. of ethylene that reacted	Yield of butene (%)		Yield of higher hydrocarbons (%)	
	Expt.					on ethylene passed	on ethylene that reacted	on ethylene passed	on ethylene that reacted
255-1	1-2*		30	32.5	87.7-80.0	46.2-43.8	52.6-54.8	23.8-20.7	27.2-25.9
255-2	1-2*		15	18.0	64.8-58.5	42.3-39.1	65.3-65.8	12.2-11.9	18.8-20.0
255-3	1-2*		10	11.6	50.2-35.9	36.5-28.2	72.6-78.6	9.0-6.0	18.0-16.8
255-4	1		5	6.2	30.0	20.9	70.4	3.9	13.3

* Before this experiment the catalyst was regenerated in a stream of air at 450° for one hour.

TABLE 7

Catalyst	Number of		Vol. of catalyst (ml)	Time of contact (sec)	Amt. of ethylene that reacted	Yield of butene (%)		Yield of higher hydrocarbons (%)	
	Expt.					on ethylene passed	on ethylene that reacted	on ethylene passed	on ethylene that reacted
122	1-2		40	1.3	80.8-46.0	32.4-9.1	40.2-56.4	24.6-6.0	30.5-37.2
138	1-2		2.5	2.6	50.0-45.6	29.0-6.9	64.0-44.2	4.2-2.0	8.9-12.8
163	1-2		1-40	1.2	32.0-18.2	17.8-3.7	56.0-20.5	5.1-2.9	16.0-15.8

In Table 6 and Fig. 3 the results are given of the work of Catalyst 255, which was prepared by precipitation with ammonia from nickel nitrate on a carrier of KSK silica gel (Sample 3) with an addition of alumina [6]. The catalyst was tested at 300°. All four samples of Catalyst 255 were of the same preparation and differed only in volume. The linear velocity of the gas was kept constant in these experiments.

Table 7 gives results on the work of a formate-impregnation catalyst; the carrier was a finely spherical aluminum silicate. In these experiments the linear velocity of the gas was kept constant and the volume of catalyst was varied; the reaction temperature was 300°.

Table 4 shows that with increase in the time of contact by a factor of 1.4-1.8, brought about by varying the linear velocity, the conversion of ethylene increased by a factor of 3-3.7 and the yield of butene (% on ethylene passed) by a factor of 2-4. With a time of contact of 3.5 seconds, the yield of dimer was 79% on the ethylene that reacted, whereas with a time of contact of 5.5 seconds it was only about 60%. With reduction of the time of contact but maintenance of the linear velocity constant there was a tendency for the conversion of ethylene to fall: 89.0-57.5% for a time of contact of 12 seconds, 56.0-32.8% for 6 seconds, and 34.5-19.9% for 3 seconds. The yield of dimer on the ethylene passed changed correspondingly. As regards dimer, the productivity of the catalyst increased with reduction of the time of contact. From the results in Tables 6 and 7 the same tendency can be seen: with reduction of time of contact with preservation of linear velocity the yield of dimer on the ethylene passed again rises. It will be seen from the results that it is preferable to carry out the reaction with a time of contact of 2.5 seconds.

SUMMARY

1. An investigation was made of the effect of temperature on the polymerization of ethylene in presence of nickel catalysts prepared in different ways. For a time of contact of 6-7 seconds the optimum temperature range is 275-300°.
2. An investigation was made of the effect of time of contact with and without maintenance of a constant linear velocity of the original gas, and it was shown that reduction in the time of contact leads to reduction in the conversion of ethylene and increase in the selectivity of the catalyst with respect to dimerization. The optimum time of contact is about 2.5 seconds.

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ULTRAVIOLET ABSORPTION SPECTRA OF SOME PYRIDINE AND NICOTINE DERIVATIVES

COMMUNICATION 4. ABSORPTION SPECTRA OF N-OXIDES OF NICOTINE AND N-METHYLANABASINE*

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In the N-oxides of ditertiary diamines of the nicotine type we have links of oxygen with nitrogen atoms of different chemical nature. This peculiarity is reflected in their chemical behavior [2], particularly in the different stabilities of the two N→O bonds toward reducing agents [3]. In this connection it was of interest to make a more detailed study of some of the physical properties of such N-oxides, particularly those which could be linked with their reactivities or could be used as a characterization of this type of compound. In the present investigation we have determined the ultraviolet absorption spectra of the N-oxides of nicotine and N-methylanabasine; we shall later publish the results of polarographic and other measurements.

TABLE 1

Solvent	λ_{\max} (m μ)	log ϵ_{\max}	Authors
Water	260	3,43	Our data **
Ethanol	260	3,45	» »
0,1 N ethanolic HCl	260	3,70	» »
0,1 N aqueous HCl	260	3,73	» »
Ethanol	260	3,48	Setkina, Danyushevskii and Gol'dfarb [4]
Ethanol	260	3,37	Lowry and Gore [5]

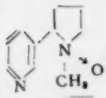
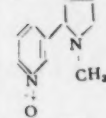
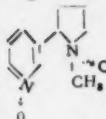
*The spectra were determined on an SF-4 spectrophotometer.

EXPERIMENTAL

In order to obtain comparable data, we decided to redetermine the spectrum of nicotine, which has been previously described in the literature [4, 5]. In water and alcohol it has an absorption band with a maximum at 260 m μ , and this retains its position in an acid medium, though with a somewhat increased extinction coefficient (Fig. 1, Table 1).

*For Communication 3 see [1].

TABLE 2

Compound	Formula	λ_{\max} (m μ)	ϵ_{\max}	$\log \epsilon_{\max}$
Nicotine PI-N-oxide		260	2 512	3,40
Nicotine Py-N-oxide		266	14 130	4,15
Nicotine PI, Py-dioxide		268	10 230	4,01

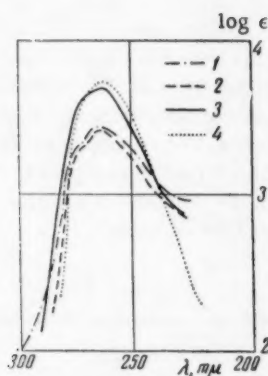


Fig. 1. Absorption curves of nicotine: 1) in ethanol; 2) in water; 3) in 0.1 N alcoholic HCl; 4) in 0.1 N aqueous HCl.

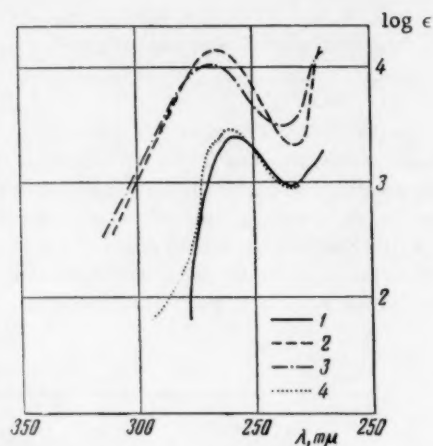


Fig. 2. Absorption curves: 1) of nicotine PI-N-oxide; 2) of nicotine Py-N-oxide; 3) of nicotine PI, Py-dioxide; 4) of nicotine (in ethanol).

As would be predicted, the absorption spectrum of the PI-N-oxide of nicotine, in which the oxygen is attached to the pyrrolidine nitrogen,* does not differ from that of nicotine itself (Fig. 2, Table 2).

A different relation is found when the absorption spectrum of nicotine is compared with that of its Py-N-oxide. In this case we observe a slight shift in the absorption maximum toward the visible region and a large increase in ϵ_{\max} . In view of our previous statement it is not unexpected that the absorption spectrum of the PI, Py-dioxide of nicotine is found to be identical with that of the Py-monoxide.

Hence, when the unshared pair of electrons of the nitrogen of the pyridine ring links up with an oxygen atom with formation of the N-oxide, there is a considerable increase in the intensity of the absorption, whereas on formation of a nicotinium ion in an acid medium ϵ_{\max} increases to a much smaller extent. Here, therefore

*The symbols PI, Py, and Pi are used to indicate substitution in the pyrrolidine, pyridine, and piperidine nuclei respectively. — Publisher.

TABLE 3

Compound	Formula	λ_{\max} (m μ)	ϵ_{\max}	log ϵ_{\max}
Anabasine		260*	2 741	3,44
N-Methylanabasine		260	2 486	3,40
N-Methylanabasine Pi-N-oxide		254 260 266	2 570 2 690 1 990	3,41 3,43 3,30
N-Methylanabasine Py-N-oxide		268	13 260	4,12
N-Methylanabasine Pi, Py-dioxide		268	11 600	4,06

*For data in literature see [7].

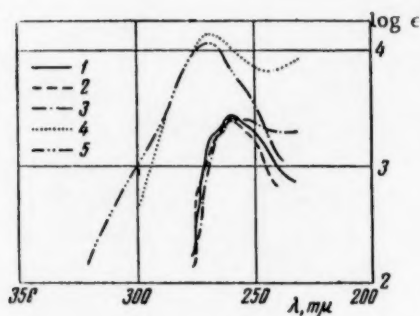


Fig. 3. Absorption curves: 1) anabasine; 2) N-methylanabasine; 3) N-methylanabasine Pi-N-oxide; 4) N-methylanabasine Py-N-oxide; 5) N-methylanabasine Pi, Py-dioxide (in ethanol).

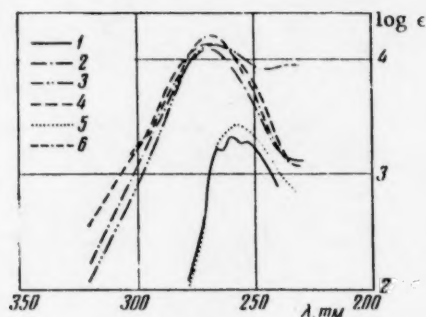
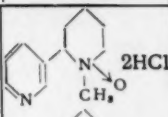
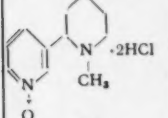
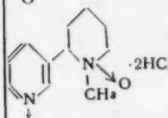
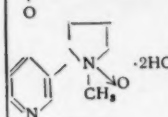
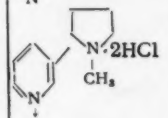
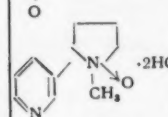


Fig. 4. Absorption curves of dihydrochlorides of: 1) N-methylanabasine Pi-N-oxide; 2) N-methylanabasine Py-N-oxide; 3) N-methylanabasine Pi, Py-dioxide; 4) nicotine Py-N-oxide; 5) nicotine Pi-N-oxide; 6) nicotine Pi, Py-dioxide (in ethanol).

we find the same behavior as in the case of pyridine and its N-oxide. Jaffe [6] explains this on the view that pyridine N-oxide has a longer conjugated system than the pyridinium ion. It is quite possible that such inclusion of oxygen in the conjugated chain is associated with the already mentioned high stability of the N→O link in the pyridine ring toward reducing agents.

TABLE 4

Compound	Formula	λ_{\max}	ϵ_{\max}	$\log \epsilon_{\max}$
N-Methylanabasine Pi-N-oxide dihydrochloride		254 260 266	2 000 2 230 1 700	3,30 3,35 3,23
N-Methylanabasine Py-N-oxide dihydrochloride		268	12 400	4,09
N-Methylanabasine Pi, Py-dioxide dihydrochloride		268	14 000	4,15
Nicotine Pi-N-oxide dihydrochloride		259	2 818	3,45
Nicotine Py-N-oxide dihydrochloride		268 221	12 590 7 943	4,10 3,90
Nicotine Pi, Py-dioxide dihydrochloride		268 220	15 850 12 590	4,20 4,10

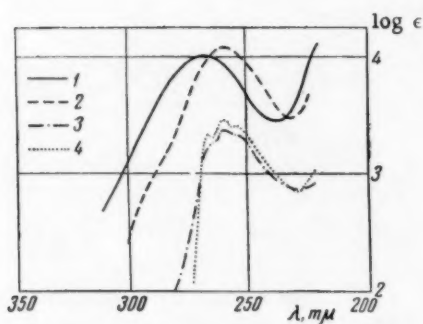


Fig. 5. Absorption curves of the Pi, Py-dioxide and Pi-N-oxide of nicotine: 1) and 3) in alcohol; 2) and 4) in water.

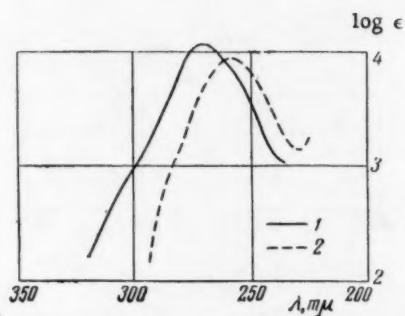


Fig. 6. Absorption curves of N-methylanabasine Pi, Py-dioxide: 1) in alcohol; 2) in water.

The absorption of anabasine, N-methylanabasine, and N-oxides of N-methylanabasine is illustrated in Fig. 3 and Table 3. Here there is almost complete coincidence of the curves for the first two of these compounds and N-methylanabasine Pi-N-oxide. The Py-N-oxide and Pi, Py-dioxide of N-methylanabasine, in full accord with the position for the analogous nicotine N-oxides, give an absorption band in which λ_{\max} is somewhat displaced toward the long waves

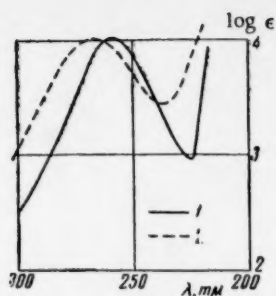
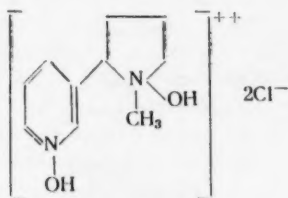


Fig. 7. Absorption curves of nicotine PI, Py-dioxide: 1) and 2) [see text; descriptions of curves (solvent used omitted in original. — Publisher].

is due to a hydrogen formed by the N→O group of the pyridine part of the molecule.

A displacement analogous to that discussed above is observed, as will be seen from Fig. 7, on examination of the absorption curve of nicotine PI, Py-dioxide in 0.1 N aqueous HCl in comparison with the curve for ethanol. In this case the displacement is associated with the formation of a salt of the type



As would be expected, the formation of a salt at the N-oxide bond of the pyrrolidine ring in nicotine PI-N-oxide does not result in a similar displacement (see Table 1).

SUMMARY

Comparison of the ultraviolet spectra of nicotine, N-methylanabasine, and their N-oxides shows that though the characters of the absorption of compounds containing the N-oxide group in the aromatic part of the molecule, on the one hand, and in the hydrogenated part, do not differ considerably, they are nevertheless sufficiently specific for a clear distinction to be drawn.

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BRIEF COMMUNICATIONS

THERMAL EXPLOSION OF DIETHYLNITRAMINE DINITRATE WITH PURELY CONVECTIVE HEAT TRANSFER

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Not only the kinetics of the chemical reaction, but also heat transfer into the surrounding medium plays an important part in thermal explosion. Heat-transfer problems are of particular importance in the study of thermal explosion of liquid and molten explosives. As was shown previously [1], in this case there is complex convective heat transfer, in which heat is transferred both as a result of heat conductance and by direct movement of the final volumes of liquid. The limiting cases are purely conductive heat transfer and purely convective heat transfer in which the heat is removed so rapidly that there is no distribution of temperature through the liquid volume. These limiting cases are normally considered in deriving a theory of thermal explosion; their experimental realization is of interest as a starting point for a detailed study of complex convective heat transfer. The convective limiting case may be achieved by intensive mixing of the substance. By achieving a state with no temperature distribution, we satisfy the basic premise of the existing nonstationary theory of thermal explosion, according to which the temperature throughout the whole of the reaction volume is the same and the whole of the temperature gradient is localized in the walls of the vessel. In this case, one may therefore expect good agreement between theory and experiment.

EXPERIMENTAL

In our experiments we used the procedure which the authors developed previously [1] for determining the critical conditions of thermal explosions with the addition of a device for stirring the substances (Fig. 1). The experiments were carried out in glass vessels of various diameter. The stirrers were made of stainless steel as special kinetic experiments showed that the rate of decomposition of the substance investigated was independent of the presence of stainless steel. To prevent distortion of the surface of the stirred substance, the axis of the stirrer was not at the center of the vessel, but at a distance of 1/3 of a diameter from the wall. The temperature distribution through the substance was eliminated by the choice of appropriate stirrer rates. Over the range of rates chosen heating of the substance was independent of the stirrer rate.

Since the whole of the thermal resistance is at the wall with purely convective heat transfer, the heat-transfer coefficient through the wall of the vessel is of considerable importance. We determined the heat-transfer coefficients by the method used in heat physics, which consists of providing an artificial source of heat under conditions close to those in the experiment. These values agreed well with those calculated by the formula $\alpha = \lambda_{gl}/d_{gl}$, where λ_{gl} is the thermal conductivity coefficient of glass and d_{gl} is the wall thickness. The temperature dependence of α , determined by the same method, also agreed with the calculated one.

Diethylnitramine dinitrate (DINA) [2-5] is a convenient subject for the investigation of thermal explosion in the liquid phase; its melting point is 52.5°. The decomposition of DINA obeys an equation of the first order [5]. DINA has a low condensed residue; the degree in change in volume at complete decomposition which we introduced previously [6, 7], is given by the following equation:

$$\mu = \frac{V_{\text{init.}} - V_{\text{fin.}}}{V_{\text{init.}}} = 0,95.$$

This leads to the fact that the heat-input term in the heat balance equation has the same form as for a zero order reaction. In actual fact, the rate of heat evolution per unit volume is given by the following equation [7]:

$$q = \frac{Q}{1 - \mu\eta} \cdot \frac{d\eta}{dt},$$

where Q is the heat effect of the reaction and η is the degree of conversion. In our case

$$\frac{d\eta}{dt} = k_0 e^{-\frac{E}{RT_0}} \cdot e^{\theta} (1 - \eta),$$

where k_0 is the pre-exponent, E is the activation energy, $\theta = \frac{E}{RT_0^2} (T - T_0)$ is the heat evolution, and T_0 is the temperature at the outer surface of the wall. Hence, it is obvious that when $\mu \rightarrow 1$

$$q = Q k_0 e^{-\frac{E}{RT_0}} \cdot e^{\theta},$$

i.e., heat evolution per unit volume obeys a zero order equation. Thus, with purely convective heat transfer, DINA corresponds to the simplest model for which Semenov's theory was derived [8,9], as in this case the basic premises of this theory, namely, the zero order of the reaction and the absence of a temperature distribution, are fulfilled.

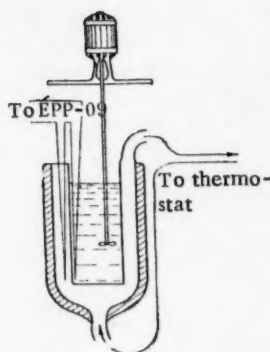


Fig. 1

In our experiments, the temperature at the outer wall of the vessel T_0 was maintained by circulation of a heat-transfer material (glycerol), which was thermostatted with an accuracy of $\pm 0.1^\circ$. The heating of the substance was measured with a copper-constantan thermocouple, one junction of which was immersed in the substance in a glass capillary and the other, in the thermostat. The change in heating with time was recorded with a ÉPP-09 potentiometer. As has been shown above, the rate of heat evolution per unit volume for DINA is independent of the degree of conversion and therefore it was expected that the heating-time curves would be close to the theoretical form of a zero order reaction, i.e., a fast increase in heating up to a definite value followed by a section in which heating is either independent or at least depends only slightly on time. This was confirmed well by experiment. The critical temperatures were determined by the usual method [1] with an accuracy of $\pm 0.5^\circ$. Determinations of the critical conditions were carried out for 5 different diameters. The results are given in the table. The critical temperatures for the same diameters were calculated by Semenov's formula [8]

$$\frac{E}{RT_0^2} - Q k_0 e^{-\frac{E}{RT_0}} = \frac{\alpha S}{V \cdot e}$$

where S is the surface area, V is the volume of substance, α is the heat emission coefficient, and R is the gas constant. As the table shows, there was good agreement between theory and experiment. The discrepancy did not exceed two degrees. The activation energy ($E = 4500$ cal/mole), the pre-exponent ($k_0 = 3.8 \cdot 10^{18}$ 1/sec), and the heat effect ($Q = 950$ cal/cc) were determined from data on heat evolution kinetics [5].

It seemed interesting to compare the critical heating with the theoretical value $\Delta T = RT_0^2/E$, which has not been done previously. As the table shows, the experimental results agreed well with the calculated values.

Charge diameter d in cm	Heat transfer coefficient of vessel $\alpha_{gl}, \text{cal/cm}^2 \cdot \text{deg} \cdot \text{sec}$	Ratio of length to diameter, l/d	Charge mass m , g	Critical temp., °C		Pre-explosion heat-ing, °C	
				calc.	from experiment	calc. $\Delta T = \frac{RT_2}{E}$	from experiment
6,2	$1,15 \cdot 10^{-2}$	1	259	152	152	7,95	9
4,9	$1,2 \cdot 10^{-2}$	2	264	154	153	8,05	8
3,75	$1,05 \cdot 10^{-2}$	2	110	156	158	8,1	8
3,65	$1,15 \cdot 10^{-2}$	2	105	157	159	8,15	10
3,2	$1,35 \cdot 10^{-2}$	2	72	160	162	8,25	9

In addition, numerical integration was used to calculate the induction period in a critical experiment (for $d = 6.2$ cm and $T_0 = 152^\circ$). Good agreement was obtained: the experimental induction period $t_{ind} = 13$ min and the calculated value $t_{ind} = 14$ min.

SUMMARY

1. A procedure was developed for studying the thermal explosion of liquid and molten explosives with purely convective heat transfer.

The critical conditions of thermal explosions of DINA (diethylnitramine dinitrate) were studied. There was good agreement of the experimental values of temperatures and heat evolution with calculated values from Semenov's theory.

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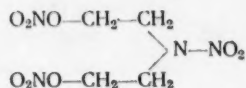
* Original Russian pagination. See C. B. translation.

KINETICS OF THERMAL DECOMPOSITION OF DIETHYLNITRAMINE DINITRATE

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The thermal decomposition of nitro compounds is a complex process, consisting of a combination of a large number of elementary acts. In most cases, a considerable part is played by autocatalysis by the final reaction products, both condensed and gaseous. Due to the complex mechanism of the process and the different effects of the final products, data obtained by different methods with the reaction carried out under various conditions frequently disagree. From the general theoretical point of view, it is of considerable interest to study reactions with the simplest kinetics by different methods. This makes it possible to approach the mechanism of decomposition with the simplest models. Diethylnitramine dinitrate (DINA) [1-3]



has a comparatively simple structure and, in analogy with ethylenedinitramine [4], could be expected to have simple liquid-phase decomposition kinetics (m.p. 52.5°).

EXPERIMENTAL

In the present work we studied the decomposition kinetics of DINA by three different methods: by gas liberation, by the change in weight, and by heat evolution. The experiments were carried out in the temperature range 150-170°. In studying the kinetics by gas liberation, we used the same procedure as in previous work [5] (in a glass vacuum apparatus with the increase in pressure determined by the compensation method). The experiments were carried out in a vessel with a volume $V = 100$ cc with 0.1-g samples. The kinetic curves were described well by an equation of the first order:

$$\frac{d\eta}{dt} = k(1-\eta),$$

where η is the degree of conversion, k is the rate constant, and t is time. Straight lines were obtained in the semilogarithmic coordinates of $\log(1-\eta)$ against t . The complete decomposition of 1 g of starting material liberated 925 cc of gas at 1 atm and 160°.

We used 0.5-g samples to study the kinetics by the change in weight. The decomposition conditions were such that the decomposition was isothermal. In this case also, straight lines were obtained in semilogarithmic coordinates. To study the kinetics of heat evolution of DINA, we used the double calorimeter described

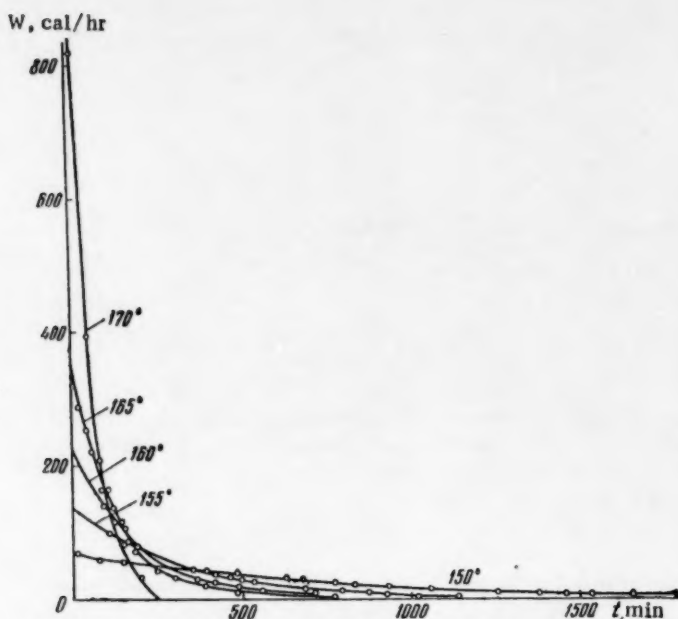


Fig. 1. Rate curves of heat evolution.

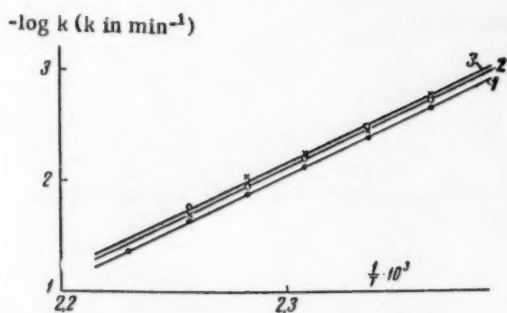


Fig. 2. Temperature dependence of reaction rate constant: 1) in a closed vessel (from gas liberation); 2) in an open vessel (from change in weight); 3) from heat evolution.

previously [6]. The experiments were carried out over the temperature range 150-170°. The rate curves of heat evolution are shown in Fig. 1. The total heat effect of thermal decomposition was found by numerical integration of the rate curve obtained. The values obtained for the heat of thermal decomposition of DINA are given in the table. As the table shows, the heat effect of the reaction increases slowly with a rise in temperature, increasing by approximately 6% over the range 150-170°. It should be noted that the heat effect of the reaction at 170° was determined with an accuracy of 4-5% as it was necessary to extrapolate a considerable section of the curve due to the high initial rate. As Fig. 1 shows, the rate of heat evolution during the thermal decomposition of DINA decreases in the course of the reaction and the maximum rate of heat evolution is reached at the very beginning of the reaction. Thus, autocatalytic decomposition, which is characteristic of many explosives, does not occur with DINA.

For all experiments we calculated the specific rate $W_{sp} = W/1-\eta$, where η is the degree of conversion determined from the heat evolution rate by the following formula:

$$\eta = \frac{\int_0^t \frac{Q}{dt} dt}{\int_0^\infty \frac{dQ}{dt} dt}$$

Temperature, °C	k · 1/min · 10 ³			Heat effect of reaction Q in cal/g
	by gas li- beration	by change in weight	by heat evolution	
150	2,07	1,8	1,65	680
155	4,14	3,4	3,53	688
160	7,29	5,96	5,65	691
165	14,3	15,0	8,95	711
170	27,0	17,0	20,0	720
Pre-exponent k ₀ , sec ⁻¹	4,8 · 10 ¹⁸	4,1 · 10 ¹⁸	3,8 · 10 ¹⁸	

The calculations showed that W_{sp} was independent of η over the whole temperature range. This confirms that the reaction is first order W_{sp} is the decomposition constant. The three methods give very similar values for the rate constants (see Table).

The temperature dependence of the reaction rate constant is shown in Fig. 2 in the coordinates $\log k$ and $1/T$, and this shows that the activation energies determined by the three methods, namely, gas liberation, change in weight, and heat evolution, were the same ($E = 45,000$ cal/mole). The values of the pre-exponent calculated for each method differed insignificantly (see Table).

SUMMARY

1. The kinetics of the thermal decomposition of diethylnitramine dinitrate were studied by three different methods: by gas liberation, by the change in weight, and by heat evolution.

2. The reaction is first order. The rate constants were determined. The activation energy and pre-exponent were calculated.

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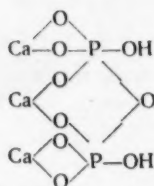
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INVESTIGATION OF THE ACIDITY OF A PHOSPHATE CATALYST AND ITS CHANGE DURING FIRING BY AN INDICATOR METHOD

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It was previously suggested that the catalytic activity of tricalcium phosphate in vapor-phase dehydration [1], hydrolysis [2], and hydration [3] is caused by its acid nature. This is confirmed by the fact that phosphate catalyzes reactions which are accelerated by acids in the liquid phase and may be deactivated by potassium carbonate [1], caustic alkali, or organic bases [4]. The acid properties of completely substituted calcium phosphate are apparently caused by the presence of chemically bound water [$\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] and its structure is schematically illustrated by the formula



Consequently, there should be a close interrelation between the acidity, catalytic activity, and the temperature at which the catalyst (crystal hydrate) is dehydrated. In connection with this, in the present work we made a quantitative study of the acidity of the phosphate catalyst and its relation to firing temperature.

EXPERIMENTAL

The catalyst was prepared by the action of an aqueous solution of calcium chloride on a dilute solution of diammonium phosphate in the presence of ammonia at 40°. The acidity of the catalyst was determined by Johnson's method, whose accuracy is $\pm 5\%$ [5]. The phosphate powder (100-200 mesh) was washed carefully with distilled water to a negative reaction for Ca^{++} , Cl^- , and PO_4^{3-} ions, which are normally adsorbed on the catalyst during its preparation and interfere with titration, then placed in a boat, dried at 100-110° in a reaction tube heated by an electric furnace, and fired for 4 hr at a definite temperature. The catalyst was titrated in a 10-15-ml tube with a ground glass stopper. Fired catalyst powder (0.5-1.0 g) was rapidly introduced into a weighed tube and the latter was hermetically sealed and weighed. To the catalyst was added 5 ml of indicator solution (2 mg of p-dimethylaminoazobenzene in 100 ml of dry isooctane) and the tube fixed in a fast shaker and shaken. The indicator was adsorbed and the white catalyst powder acquired a red color. For quantitative determination of the acidity of the catalyst, 0.1 N solution of n-butylamine in dry isooctane was gradually introduced into the tube in small portions of 0.05-0.1 ml. After 1-5 hr, as the color of the catalyst weakened, more butylamine was added and the tube shaken again. Neutralization was considered complete when the red color disappeared completely.

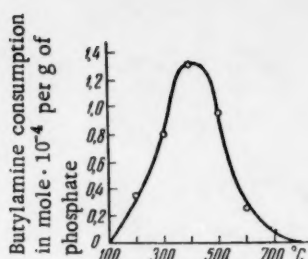


Fig. 1. Effect of firing temperature on catalyst acidity.

Titration of the sample lasted for 12-18 hr. The gradual addition of the amine reduced to a minimum the possible adsorption of the base on nonacid sections of the catalyst surface and prevented possible overtitation. At the end of the titration, the precipitate was allowed to settle, the solution decanted, and the excess amine titrated with 0.05 N trichloroacetic acid in isooctane. The red color usually appeared after the addition of 2-3 drops of acid, indicating that a relative small excess of amine had been introduced. Even traces of water distorted the titration results, reducing the amine consumption. In our experiments, three samples of a given catalyst were titrated simultaneously and under the same conditions. Quite satisfactory agreement was usually obtained and the average result was taken.

Determination of the acidity of phosphate catalyst and its change during firing. It was found that carefully washed catalyst that had been dried well at 100-110° did not change the color of the indicator. After being fired at 200°, the catalyst acquired a weak pink color when treated with indicator and after firing at 400°, the color was bright red. These experiments showed that the catalyst surface actually had acid properties. We then studied the relation of catalyst acidity to firing temperature over the range 200-800° by the method given above. The results obtained are given in Fig. 1. This figure shows that with an increase in temperature, the amine consumption increased and reached a maximum at 400°. A further increase in firing temperature to 500, 600, and 700° led to an increasing fall in the amine consumption. A sample fired at 800° did not change the indicator color.

It is interesting to compare data on the relation of the acidity and catalytic activity of phosphate to its firing temperature. It was previously established that the activity of phosphate catalyst falls in the dehydration of ethanol [1] by a factor of 5 after firing at 600-700° (1 hr), in the dehydration of formic acid [1] by a factor of 2 after firing at 800° (5 hr), and in the vapor-phase hydrolysis of chlorobenzene [2] by a factor of 4-5 after firing at 850° (2 hr). On the other hand, as Kazakov showed [6], in addition to adsorbed water, tricalcium phosphate contains 0.5 mole of firmly bound water, which is removed only by firing at 400-800°. Thus, there is a symbatic relation of the acidity and activity to the firing temperature of a phosphate catalyst and to the presence of structurally bound water in it.

It may be considered that firing phosphate at temperatures below 400° leads to freeing of its acid sections from adsorbed water, which blocks the active surface of the catalyst. Therefore, undehydrated phosphate does not change to color of the indicator, while partly dehydrated phosphate (at 200°) changes it weakly. Al_2O_3 behaves analogously and it is only after firing in vacuum at 250° that it shows its acid properties and changes the color of an indicator [7]. Phosphate shows maximum acidity after firing at 400°, when probably almost all the adsorbed water is removed. Water bound structurally in the phosphate molecule causes its acid properties. The removal of this water by firing at temperatures above 500° leads to a fall in both the acidity and the activity of the catalyst. If it is assumed that one acid section is neutralized by one butylamine molecule, then the number of active centers will be $A = 6.06 \cdot 10^{23} \cdot 1.3 \cdot 10^{-4} = 7.8 \cdot 10^{19}$, where $1.3 \cdot 10^{-4}$ is the number of moles of butylamine consumed in the neutralization of 1 g of phosphate fired at 400°.

SUMMARY

1. The acidity of tricalcium phosphate was determined by an indicator method.
2. There is a similarity in the relations of the acidity and catalytic activity of phosphate to its firing temperature.
3. It was confirmed that the acid nature of a phosphate catalyst, which is responsible for its activity, is caused by structurally bound water.

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DETONATION PARAMETERS OF TRINITROTOLUENE-HEXOGEN MIXTURES

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By the method described in [1], we measured the parameters of the detonation wave in a Chapman-Juge plane for mixtures of trinitrotoluene with various amounts of hexogen. Ground trinitrotoluene with a mean particle size of 0.1 mm and civil hexogen were used for preparing the mixtures. The diameter of the charges was 40 mm and the length together with the explosion lens forming the planar front was 85 mm. The experimental data obtained are given in the table, where ρ_0 is the initial density of the mixture, D is the detonation rate, U is the velocity of the explosion products, P is the pressure, and n is the polytropy index of the explosion products close to the Chapman-Juge plane.

In [1] it was shown that n does not change with a change in the initial density of the explosive. This means that the value of n together with the detonation rate D, which normally is readily measured by various methods, make it possible to calculate all the other mechanical parameters, not only at the front of the detonation wave, but also the distribution of these parameters at some distance behind the front [2]. In the given work, it was established that if the polytropy indices of the explosion products of trinitrotoluene (T) and hexogen (H) are known, then the polytropy index for a mixture of these substances may be calculated by the formula:

$$n_{TH} = xn_T + (1 - x)n_H \quad (1)$$

where x is the trinitrotoluene content in percent. The last column of the table gives the values of n_{TH} , calculated by formula (1). As the table shows, these values agree well with the experimental data. The result obtained is apparently accurate for other mixtures of substances.

Composition: TNT/hexogen	ρ_0 in g/cc	D in km/sec	U in km/sec	P · 10 ⁹ in bars	n	n_{TH}
100/0*	1,59	6,94	1,83	202	2,79	—
75/25	1,65	7,31	1,96	236	2,73	2,74
50/50	1,68	7,65	2,07	266	2,70	2,69
25/75	1,71	8,12	2,23	310	2,64	2,64
0/100*	1,755	8,66	2,41	366	2,59	—

* Data published in [1].

SUMMARY

The polytropy index of the explosion products for trinitrotoluene-hexogen mixtures may be calculated from the known values of this index for the individual components.

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ADDITION OF CARBON TETRACHLORIDE TO BUTADIENE AND PIPERYLENE

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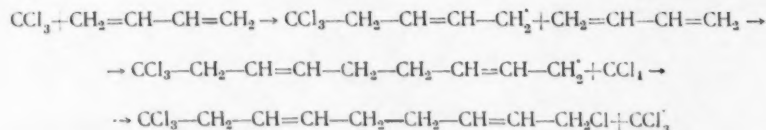
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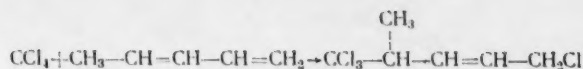
Kharasch and his co-workers [1] found that carbon tetrachloride adds to olefins under the action of peroxide catalysts and ultraviolet light. In a footnote in the article of Kharasch, Freiman, and Urry [2] on the addition of trichlorobromomethane to butadiene sulfone it was reported that trichlorobromomethane adds to butadiene by 15-20% in the 1,2 position and 80-85% in the 1,4 position. In the same article, the authors stated that the action of CCl_4 on butadiene sulfone in the presence of benzoyl peroxide gave 12% of a sulfur-free adduct, consisting of a mixture of 1,1,1,5-tetrachloro-2-pentene and 1,1,1,3-tetrachloro-1-pentene. The following data were given for this fraction: b.p. 76-79° (5 mm); 127-129° (60 mm); n_D^{20} 1.5060. The preparation of 1,1,1,5-tetrachloro-3-pentene by the action of carbon tetrachloride on butadiene sulfone in the presence of benzoyl peroxide is described in a British patent [3]. The following constants were given for the product obtained (yield 19% of theoretical): b.p. 129-130° (60 mm); d_4^{25} 1.3778; n_D^{25} 1.5068.

We carried out experiments on the addition of carbon tetrachloride to butadiene and piperylene under the action of benzoyl peroxide. The reaction was carried out by heating butadiene with CCl_4 in an autoclave at 120-130° and was accompanied by strong tar formation. Three products were isolated by distillation of the reaction products. We obtained a very small amount of a low-boiling product with b.p. 61-63° (7 mm); n_D^{20} 1.4874; d_4^{20} 1.2110, which corresponded in analysis to the composition $\text{C}_5\text{H}_4\text{Cl}_2$ (calculated Cl 52.6%; found Cl 52.4%). The substance contained a $\text{CH}_2 = \text{CH}-$ group as it gave formaldehyde on ozonization and was evidently the product of elimination of two molecules of hydrogen chloride from the addition product of butadiene. The substance was not investigated in detail. The main product was 1,1,1,5-tetrachloro-3-pentene (yield ~15% of theoretical); b.p. 83-84° (7 mm); n_D^{20} 1.5068; d_4^{20} 1.3769; found MR 44.83; $\text{C}_5\text{H}_5\text{Cl}_4\text{F}$. Calculated MR 44.29.

The third product (yield 6.4% of theoretical) had b.p. 132-134° (7 mm); n_D^{20} 1.5111; d_4^{20} 1.2480; found MR 62.94. $\text{C}_9\text{H}_{12}\text{Cl}_4\text{F}_2$; calculated MR 62.29; the third product was produced by the addition of CCl_4 to two molecules of butadiene. Its structure was shown to be that of 1,1,1,9-tetrachloro-3,7-nonadiene by oxidation with potassium permanganate. This yielded succinic acid. The formation of 1,1,1,9-tetrachloro-3,7-nonadiene may be represented by the following scheme:



In the addition of CCl_4 to piperylene (mixture of cis and trans isomers), only one product was isolated in a pure form (yield 12.5% of theoretical) and this had b.p. 103-105° (15 mm); n_D^{20} 1.4960; d_4^{20} 1.3086; found MR 49.58. $\text{C}_6\text{H}_8\text{Cl}_4\text{F}$. Calculated MR 48.91. A study of the structure of this product showed that it was 1-chloro-4-methyl-5,5,5-trichloro-2-pentene (formation of chloroacetic acid by oxidation with potassium permanganate); the addition of CCl_4 to piperylene consequently occurs in the 1,4 position:



EXPERIMENTAL

Addition of CCl_4 to butadiene. For the reaction we used 100 ml of butadiene, 400 ml of CCl_4 , and 3 g of benzoyl peroxide. The reaction was carried out in an autoclave at 120-130° for 11 hr. When the autoclave was opened, a small amount of HCl was liberated and the reaction mixture had a dark color. The reaction product was washed with water and alkali solution and dried over calcium chloride. After removal of the CCl_4 , the residue was vacuum distilled. Several distillations yielded the following products:

1) A product with b.p. 61-63° (7 mm); weight 2.05 g; n_D^{20} 1.4874; d_4^{20} 1.2110; 2) a product with b.p. 83-84° (7 mm); weight 32.7 g; n_D^{20} 1.5068; d_4^{20} 1.3769; found MR 44.89. $\text{C}_5\text{H}_6\text{Cl}_4\text{F}$. Calculated 44.29; found Cl 67.90%; calculated Cl 68.27%. 3) a product with b.p. 132-134° (7 mm); weight 10.12 g; n_D^{20} 1.5111; d_4^{20} 1.2480; found MR 62.94. $\text{C}_9\text{H}_{12}\text{Cl}_4\text{F}_2$. Calculated MR 62.29; found Cl 54.64%; calculated Cl 54.20%.

Addition of CCl_4 to piperylene. For the reaction we used 120 ml of piperylene, 500 ml of CCl_4 , and 1 g of benzoyl peroxide. The reaction was carried out in an autoclave at 90-100° for 8 hr. The reaction mixture was treated as in the case of butadiene.

As a result of several distillations, we isolated a product with b.p. 103-105° (15 mm); n_D^{20} 1.4960; d_4^{20} 1.3006; found MR 49.58. $\text{C}_6\text{H}_8\text{Cl}_4\text{F}$. Calculated MR 48.91; found Cl 64.31%; calculated Cl 63.96%. The residue was 105 g of tar.

Determination of the structure of 1,1,1,9-tetrachloro-3,7-nonadiene by oxidation with potassium permanganate in a neutral medium. For the oxidation we used 10 g of the product examined and 32 g of potassium permanganate. Dry potassium permanganate was added in small portions to a vigorously stirred aqueous emulsion of the product. A fresh portion was added when the solution had been completely decolorized. The manganese dioxide precipitate was removed by filtration and boiled twice with water. The filtrates were combined and evaporated until a concentrated solution of salts was obtained. The solution of salts was acidified to Congo. On standing, the solution deposited a white precipitate; it was collected and recrystallized from water to yield coarse, regular crystals with m.p. 181-182°. A mixture with succinic acid had m.p. 182°.

Determination of the structure of 1,1,1,5-tetrachloro-2-methyl-3-pentene by oxidation with potassium permanganate in a neutral medium. For the oxidation we used 10 g of 1,1,1,5-tetrachloro-2-methyl-3-pentene and 15 g of potassium permanganate. The oxidation was carried out as in the previous experiment, but the filtrate was extracted with ether after evaporation and acidification. The ether extract was dried with sodium sulfate. After removal of the ether, the residue was distilled from a small flask. We isolated 2.5 g of a fraction with b.p. 180-185°, which crystallized. The melting point was 60°, which corresponds to chloroacetic acid. A mixed melting point was 61°.

SUMMARY

1. The addition of carbon tetrachloride to butadiene and piperylene was studied.
2. The addition of carbon tetrachloride to butadiene and piperylene occurs in the 1,4 position.
3. In the case of carbon tetrachloride and butadiene, we also isolated the product from the reaction of two molecules of butadiene with one molecule of carbon tetrachloride.

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VIBRATION FREQUENCIES OF Si-H and Si-D BONDS AND THE ELECTRONEGATIVITY OF SILYL GROUPS

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In a series of papers [1-4], we have already pointed out the relation of the vibration frequencies of Si-H and Si-D bonds to the nature of the atoms and groups attached to the silicon. As was established by Smith and Angelotti [5], there is no clear general relation between the vibration frequencies of Si-H bonds and the sum of the electronegativities (according to Gordy) of the atoms attached to the silicon. Much better results in this direction may be obtained by using group electro negativities. One method of determining group electronegativities from vibrational frequencies was proposed in 1958 by Wilmshurst [6]. However, he did not use the empirical equation he proposed for determining the electronegativities of silyl and germyl groups. As we established, silanes

TABLE 1

Silane R_3Si-H	ν^* Si-H in cm^{-1}	Electronegativity of X_3Si group		Magnitude of effect of atoms or organic radicals present in given silyl group	
		"effec- tive" $-X_s$	- X by [6]	Si-R bond	value
Cl_3Si-H	2258,3	2,234	2,242	Si-Cl	0,745
$(C_6H_5)_3Si-H$	2126,0	2,103	2,100	Si- C_6H_5	0,701
$(CH_3)_2(C_6H_5)Si-H$	2120,5	2,097	2,092	Si- CH_3	0,698
$(CH_3)(F)_2Si-H$	2227,5	2,204	2,204	Si-F	0,753
$(C_2H_5)_3Si-H$	2098,0	2,075	2,066	Si- C_2H_5	0,692
Br_3Si-H	2236,0	2,212	2,223	Si-Br	0,737
$(C_3H_7)(Cl)_2Si-H$	2205,7	2,182	2,187	Si- C_3H_7	0,693
$(i-C_3H_7)(Cl)_2Si-H$	2199,9	2,176	2,180	Si- C_3H_7-i	0,687
$(C_6H_5)(H)_2Si-H$	2158,3	2,135	2,131	Si-H	0,717
$(CH_2=CH)(C_6H_5)(CH_3)Si-H$	2123,8	2,101	2,095	Si- $CH=CH_2$	0,702
$(CH_2=CHCH_2)(CH_3)Si-H$	2212,0	2,188	2,193	Si- $CH_2-CH=CH_2$	0,699
$(ClCH_2)(CH_3)(H)Si-H$	2156,0	2,133	2,127	Si- CH_2Cl	0,717
$(p-ClC_6H_4)(CH_3)(H)Si-H$	2144,7	2,121	2,120	Si- C_6H_4Cl-p	0,706
$(m-ClC_6H_4)(CH_3)(H)Si-H$	2142,0	2,119	2,117	Si- C_6H_4Cl-m	0,704
$(CH_3O)_3Si-H$	2203,2	2,179	2,182	Si- OCH_3	0,726
$(C_2H_5O)_3Si-H$	2196,0	2,174	2,177	Si- OC_2H_5	0,724
$(i-C_3H_7O)_3Si-H$	2190,8	2,172	2,173	Si- OC_3H_7-i	0,722
$(C_6H_{11})(C_6H_5)(H)Si-H$	2125,0	2,109	2,100	Si- C_6H_{11}	0,684
$(C_6H_{11})(Cl)_2Si-H$	2205,7	2,182	2,188	Si- C_6H_{11}	0,693
				Si- C_4H_9	(0,693)**
$(i-C_4H_9)(CH_3)(H)Si-H$	2135,0	2,112	—	Si- C_4H_9-i	0,697

*Data taken from [5].

**Assumed.

are no exception in this respect. This is demonstrated conclusively by the data in Table 1.

TABLE 2

Hydride or deuteride	X_c	Frequency of Si-H bond in cm^{-1}		Δ	Literature re- ference	
		exp.*	calc.			
Hydrides						
H_2SiCl_2	2,207	2229,3	2231,3	-2,0	[4]	
$(\text{CH}_3)_2(\text{Cl})\text{SiH}$	2,141	2168,2	2164,6	+3,6	[4]	
$(\text{CH}_3)_2\text{SiH}_2$	2,113	2135,2	2136,2	-1,0	[4]	
$(\text{C}_6\text{H}_5)(\text{Cl})_2\text{SiH}$	2,191	2212,3	2215,1	-3,2	[4]	
$(\text{C}_6\text{H}_5)(\text{CH}_3)(\text{Cl})\text{SiH}$	2,144	2170,2	2167,6	+2,6	[4]	
$(\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{SiH}$	2,100	2123,6	2123,1	+0,5	[4]	
$(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{SiH}_2$	2,116	2140,7	2139,3	+1,4	[4]	
$(\text{C}_6\text{H}_5)_2\text{SiH}_2$	2,119	2142,7	2142,3	+0,3	[4]	
$(\text{C}_6\text{H}_5)_2(\text{Cl})\text{SiH}$	2,147	2168,2	2170,6	-1,6	[4]	
$(\text{C}_6\text{H}_5)_2(\text{CH}_2=\text{CH})\text{SiH}$	2,104	2128,0	2127,1	+0,9	[4]	
$(\text{C}_6\text{H}_5)(\text{CH}_2=\text{CH})(\text{Cl})\text{SiH}$	2,148	2169,5	2171,6	-2,1	[4]	
$(\text{C}_2\text{H}_5)_2(\text{CH}_2=\text{CH})\text{SiH}$	2,086	2108,3	2108,9	-0,6	[4]	
$(\text{C}_2\text{H}_5)_2(\text{Cl})\text{SiH}$	2,129	2152,7	2152,4	+0,3	[4]	
$\text{C}_2\text{H}_5\text{Si}(\text{Cl})_2\text{H}$	2,182	2205,8	2206,0	-0,2	[4]	
$(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{SiH}$	2,082	2103,4	2104,9	-1,5	[4]	
$(\text{CH}_3)(\text{C}_2\text{H}_5\text{O})_2\text{SiH}$	2,140	2165,2	2163,5	+1,7	[4]	
$(m\text{-ClC}_6\text{H}_4)_2\text{SiH}_2$	2,138	2162,6	2161,5	+1,1	[4]	
$(\text{CH}_3)(\text{Cl})_2\text{SiH}$	2,189	2213,5	2213,1	+0,4	[4]	
$\text{C}_6\text{H}_{13}\text{SiH}_3$	2,127	2152	2150,4	+1,6	[1]	
$(\text{C}_6\text{H}_7)_2\text{SiH}_2$	2,103	2127	2126,1	+0,9	[1]	
$(\text{C}_6\text{H}_5)(\text{Br})_2\text{SiH}$	2,175	2193	2198,9	-4,1	[7]	
$(\text{C}_6\text{H}_5)(\text{Br})\text{SiH}_2$	2,155	2177	2178,7	-0,3	[7]	
$(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2\text{SiH}_2$	2,110	2132	2133,2	-1,2	[7]	
$(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_7)\text{SiH}_2$	2,111	2132	2134,2	-2,2	[7]	
$(\text{C}_6\text{H}_5)(\text{C}_4\text{H}_9)\text{SiH}_2$	2,111	2132	2134,2	-2,2	[7]	
$(\text{C}_6\text{H}_5)(i\text{-C}_3\text{H}_7)\text{SiH}_2$	2,105	2129	2128,2	+0,8	[7]	
$(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_{13})\text{SiH}_2$	2,102	2129	2125,1	+3,9	[7]	
SiH_4	2,151	2175	2174,7	+0,3	[1]	
Br_2SiH_2	2,191	2219	2215,1	+3,9	[8]	
$(\text{CH}_3)_2\text{SiH}$	2,094	2118	2117,0	+1,0	[9]	
$(\text{CH}_3)(\text{F})\text{SiH}_2$	2,168	2185	2191,8	-6,8	[10]	
$(\text{C}_2\text{H}_5)_2\text{SiH}_2$	2,101	2130	2124,1	+5,9	[3]	
$(\text{C}_2\text{H}_5)(\text{CH}_2=\text{CH})\text{SiH}_2$	2,111	2136	2134,2	+1,8	[2]	
$(\text{CH}_2=\text{CHCH}_2)_2(i\text{-C}_4\text{H}_9)\text{SiH}$	2,095	2120	2118,0	+2,0	[2]	
$(\text{CH}_2=\text{CHCH}_2)_2(\text{CH}_3)\text{SiH}$	2,096	2125	2119,1	+5,9	[2]	
Deuterides						
$\text{C}_6\text{H}_5\text{SiDCl}_2$	2,182	1608	1604	+4,0	Present work (Raman spectrum)	
$(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{SiD}$	2,082	1527	1528	-1,0		
$\text{C}_6\text{H}_{13}\text{SiD}_3$	2,127	1560**	1561	-1,0		[3]
$(\text{C}_2\text{H}_5)_2\text{SiD}_2$	2,101	1548**	1542	+6,0		[3]
$(\text{C}_2\text{H}_5)_3\text{SiD}$	2,075	1530	1523	+7,0		[3]

* In Raman and infrared spectra.

** Mean value of symmetrical and antisymmetrical vibrations.

If the data obtained are plotted on a graph, then with insignificant deviations, all lie along a line whose equation has the form

$$\nu_{\text{Si-H}} = 1011 \cdot X_c \quad (1)$$

This transposition of Wilmshurst's equation makes it easy to determine the mean values of the electronegativities of silyl groups from the frequencies presented in Table 1; they hardly differ from the electronegativities of silyl groups found from Wilmshurst's equation, but contrary to the latter, they make it possible to obtain more accurate values of the vibration frequencies when the problem is reversed. In contrast to the group electronegativities according to Wilmshurst (X), it is advantageous to call them "effective" electronegativities of silyl groups (X_s), for though they are derived with allowance for the slight effect of the mass of the silyl group, it is considered to a lesser extent in them than in the group electronegativities of Wilmshurst. Table 1 gives the

values of the mean ("effective") electronegativities of silyl groups. On the other hand, this equation makes it possible to determine the vibration frequencies of Si-H bonds in other silanes if the electronegativities of the silyl groups are known. The latter are readily found if the "effective" electronegativity is regarded as the sum of the effects of three atoms or organic radicals present in the given silyl group. Table 1 gives the magnitudes of the effects of the corresponding atoms and organic radicals found in this way.

By using the data in Table 1, it is easy to determine the "effective" electronegativity of any silyl group containing the given atoms or organic radicals. By substituting these in equation (1), it is possible to determine the required value of the vibration frequency of the Si-H bond with quite a high accuracy. This is conclusively demonstrated by the data in Table 2.

As Table 2 shows, the vibration frequencies for hydrides found by the proposed empirical equation (1) deviate from the experimental values by an average of $\pm 2-4 \text{ cm}^{-1}$. This is quite satisfactory if we consider the natural deviations in experimental frequencies found in the literature.

For deuteriosilanes (see Table 2) the empirical equation has the same form and differs only in the coefficient:

$$\nu_{\text{Si-D}} = 734 \cdot X.$$

In principle, the same relation ($\nu = A \cdot X_s$) is applicable to germanium hydrides and deuterides [4], with the only difference that for them the values of X_s will naturally be different: for Cl_3Ge —2.127; Br_3Ge —2.085; $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{Ge}$ —1.991 etc.

SUMMARY

A simple empirical relation is put forward for relating the vibration frequencies of Si-H and Si-D and also Ge-H and Ge-D bonds to the electronegativities of silyl and germyl groups.

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EFFECT OF PYRAN RING ON ACID HYDROLYSIS OF CELLULOSE

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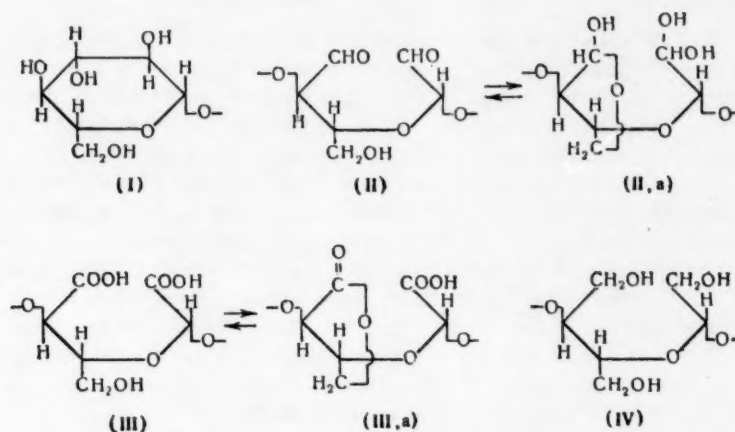
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In recent years considerable attention has been paid to the chemical nature of weak bonds in the actual molecule of cellulose [1, 2]. However, the chemical nature of acid-sensitive bonds has not yet been established unequivocally. There are few literature data on the effect of nonhydroxyl functions in the glucose unit on the stability of acetal bonds in an acid medium. It is known that carboxyl groups in position 6 [3-5] and also ketone groups in positions 2 and 3 [6] in the pyran ring do not appreciably reduce the stability of acetal bonds in an acid medium. Bearing this in mind, it seemed interesting to study the change in stability of acetal bonds in an acid medium in a cellulose molecule containing fragments with an opened pyran ring. For this purpose, we made a comparative investigation of the stability of acetal bonds in an acid medium of cellulose (I) and dialdehyde- (II), dicarboxy- (III), and dihydroxycelluloses (IV).



It should be noted that the literature contains separate reports on the possible effects of functional groups at C_2 and C_3 atoms on the stability of acetal bonds in an acid medium [7-10], but no detailed investigation in this direction has been carried out.

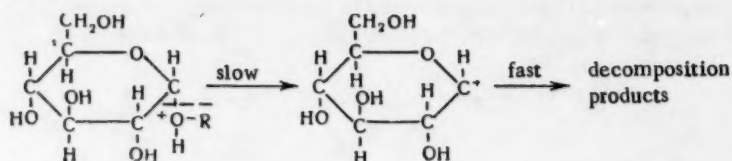
EXPERIMENTAL

Samples of dialdehyde-, dicarboxy-, and dihydroxycelluloses were obtained by literature methods [11-13]. The investigation was carried out on samples of dialdehydocellulose (11% CHO groups) and preparations of dihydroxycellulose and dicarboxycellulose (10% COOH groups) prepared from it. The stability of these samples in an acid medium was determined by the change in weight during hydrolysis in 1 N HCl at 20° (24 hr) and 98° (2 hr). Experimental data on the stability of modified celluloses is given in the table.

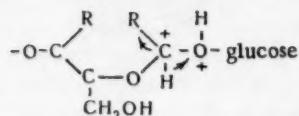
Data on Stability of Modified Celluloses in an Acid Medium

Hydrolysis conditions	Weight loss in %			
	dialdehydocellulose	dicarboxycellulose	dihydroxycellulose	cellulose
1N HCl				
20°, 24 hr.	—	0,5	26,3	—
98°, 2 hr.	28,0	30,0	30,0	0,5

From the data in the table it follows that regardless of the chemical nature of the functional groups at C₂ and C₃, the stability of preparations with structures (II), (III), and (IV) was sharply reduced in comparison with cellulose (I). From the point of view of the mechanism of acetal bond scission in an acid medium proposed by Bunton [14], the introduction into the α position of more negative substituents than hydroxyl groups, namely, carboxyl and aldehyde groups,



should hinder the displacement of the pair of electrons between O₄ and C₁ and, consequently, hamper the scission of these bonds.

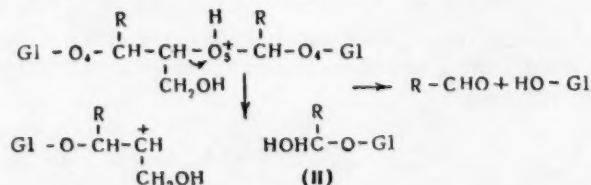


where

R: COOH : CHO : CH₂OH

The investigation of celluloses, containing in the chain fragments of the type (II), (III), and (IV), showed that the rate of their acid hydrolysis changes in the series: (IV) > (III) > (II) > (I).

These experimental data lead us to the conclusion that the pyran ring hampers the scission of acetal bonds to a greater extent than the introduction of such a strongly negative substituent as a carboxyl group into the α position. We consider that the greater instability of structures (II), (III), and (IV) in comparison with cellulose (I) is caused not so much by the functional groups as by the opening of the pyran ring. As the data in the table show, dihydroxycellulose (IV) is hydrolyzed by 1 N HCl in the cold, while cellulose (I) is hydrolyzed only at elevated temperatures. The effect of the pyran ring we discovered is confirmed by the analogous behavior of low-molecular organic compounds. For example, 1,1-dimethoxy glucose is hydrolyzed by dilute mineral acids at 40° [15], while methyl glucoside, which has a pyran ring, is hydrolyzed only on boiling. Models of methyl glucoside derivatives with an open pyran ring are much less stable than methyl glucoside [16-18]. It may be assumed that the acetal oxygen O₅ is capable of protonization in compounds with an open ring (see scheme below). Then the unstable semiacetal (II) formed by cleavage of the 1-5 bond will decompose with solution of monomeric products with aldehyde groups at C₁. This hypothesis is also supported by the fact that we did not detect an increase in CHO groups in the solid residue after hydrolysis. Using literature data [9, 19] and this fact, we put forward a hypothetical mechanism for the hydrolysis, described by the following scheme:



where R: COOH : CHO : CH₂OH

Gl is a glucose residue

The effect of the functional groups in the open pyran ring in the general form agrees with the ideas of the vicinal effect, which is determined by substituents of different degrees of negativity. As is shown by the series presented above, compounds of structure (IV), which have the less negative CH_2OH group, are hydrolyzed more rapidly than compounds of types (II) and (III).

Compounds of type (III) should be more stable than compounds of type (II) as the latter have the less negative aldehyde group. On the contrary, we showed experimentally that compounds of structure (III) are less stable. This phenomenon may be caused by a reduction in the electronegativity of the carboxyl groups due to the fact that they are not in a free state, but in the form of lactones [20] (III, a) and their dissociation in an acid medium is strongly suppressed. From the importance of the effect of opening the pyran ring at the C-C bond on the properties of the 1-4 and 1-5 acetal bonds, which we discovered, it follows that fragments (II), (III), and (IV) may be the weak positions in the chain of the cellulose molecule. We extended this conclusion on the weakening of the acetal bond in an acid medium to a pyran ring, opened due to scission of the 1-5 bond, if it exists in the cellulose molecule [21]. Thus, the stabilizing effect of the pyran ring on the 1-4 acetal bond, which we discovered, is of substantial help in the search for ways of opening the ring at the 1-5 bond for easy hydrolysis of cellulose.

SUMMARY

An effect of the pyran ring and its opening on the chemical behavior of the acetal bond was discovered.

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LETTERS TO THE EDITOR

SYNTHESIS OF DIACETYLENE MACROCYCLIC LACTONES

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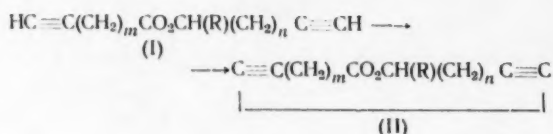
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To study routes to the synthesis of macrolides, we developed a method of preparing diacetylene macrocyclic lactones according to the scheme:



The ω, ω' -diacetylene esters (I) were cyclized at high dilution (final concentration 0.1%) in boiling 5% solution of copper acetate in a mixture of ether and pyridine (1:3) (cf. [1]). The lactones obtained were purified by chromatography on Al_2O_3 and recrystallization from hexane. By this method, the butyn-3-yl ester of undecyn-10-oic acid (I) ($m = 8, n = 1, R = H$), with m.p. 33.8–34.2° (found: C 76.96; H 9.66%) gave an 80% yield of lactone (II) ($m = 8, n = 1, R = H$), with m.p. 55.5–56° (found: C 77.62; H 8.55%), which was converted into pentadecanolid by catalytic hydrogenation. Cyclization of ester (I) ($m = 8, n = 1, R = CH_3$), with b.p. 104° (0.25 mm); n_D^{20} 1.4584, d_4^{20} 0.9219 (found: C 77.23; H 9.78%) gave a 60% yield of lactone (II) ($m = 8, n = 1, R = CH_3$) with m.p. 30.4–31.4° (found: C 78.03; H 9.10%). The ultraviolet spectra of these two lactones ($\lambda_{\text{max}}^{\text{alcohol}}$ 226, 240, 254 μ ; ϵ 720, 715, 440) were characteristic of diynes. The frequency of the CO group (ν_{max} 1724 cm^{-1}) in the infrared spectrum of (II) ($m = 8, n = 1, R = H$) was displaced in comparison with the frequency of the CO group of the corresponding acyclic ester and pentadecanolid (ν_{max} 1740 cm^{-1}) (in vaseline oil).

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POLYMERIZATION OF CYCLOOLEFINS

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We investigated the polymerization of cycloolefins (cyclohexene, 1,3-cyclohexadiene, 1-methyl-1,4-cyclohexadiene, 1,2-dimethyl-1,4-cyclohexadiene, 1-methyl-1,4-cyclohexadiene, 1,2-dimethyl-1,4-cyclohexadiene, 1,4-dimethyl-1,4-cyclohexadiene, and 1,5-dimethyl-1,4-cyclohexadiene) and also the properties of the polymers synthesized and the possibilities of their application in various fields.

The above hydrocarbons were polymerized in various solvents, at various temperatures, for various contact times, and with various catalysts and also under the action of β - and γ -radiation.

a) The use of organometallic catalysts and titanium tetrachloride gave: 1) a cyclohexene polymer with m.p. 120-125°; found: C 85.61; H 14.39%. Calculated: C 85.7; H 14.3%. 2) a 1,3-cyclohexadiene polymer with m.p. 175-185°; found: C 89.93; H 10.08%. Calculated: C 90; H 10%. 3) a 1,4-cyclohexadiene polymer with m.p. ~190°; found: C 89.98; H 10.10%. 4) polymers of 1-methyl-1,4-cyclohexadiene, 1,4-dimethyl-1,4-cyclohexadiene, 1,2-dimethyl-1,4-cyclohexadiene, and 1,5-dimethyl-1,4-cyclohexadiene containing two and more monomeric units in the chain, depending on the reaction conditions.

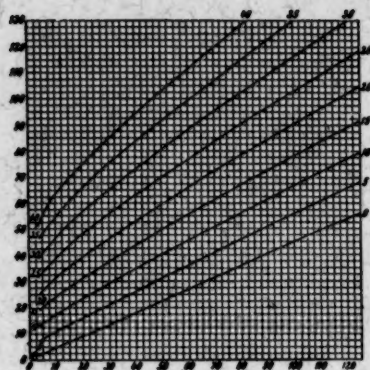
b) The use of boron trifluoride gave: 1) polymers of 1,3-cyclohexadiene with m.p. 100-220° and mol. weight 200-10,000. Found: C 89.57; H 10.57%. 2) a 1,4-cyclohexadiene polymer with m.p. ~200°. Found: C 89.91; H 10.07%. 3) a 1-methyl-1,4-cyclohexadiene polymer with m.p. 150-157° and mol. weight 820. Found: C 89.26; H 10.74%. Calculated: C 89.36; H 10.64%. 4) polymers of 1,2-dimethyl-1,4-cyclohexadiene, 1,4-dimethyl-1,4-cyclohexadiene, and 1,5-dimethyl-1,4-cyclohexadiene with two and more monomeric units in the chain.

c) Polymerization of the above hydrocarbons under the action of β - and γ -radiation formed polymers of various structures, containing two and more units in the chain. The investigation is continuing.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTl	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.



TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian



CONSULTANTS BUREAU
227 W. 17 ST., NEW YORK 11, N. Y.

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

Technicians and statisticians working with the results of hydrochemical analyses performed at different times by different laboratories inevitably face the problem of converting their figures to one system.

All such calculations are considerably simplified by the use of the tables and nomograms in this book, originally published by the State Scientific and Technical Press for Literature on Geology and the Conservation of Mineral Resources, Moscow.

All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

CONTENTS

Introduction

Tables for converting water-analysis results from one form to another

- I. Table for converting hardness, expressed in German degrees, into milligram-equivalents
- II. Table for converting milligram-equivalents of Ca^{2+} , Mg^{2+} and HCO_3^- into German degrees of hardness
- III. Tables for converting milligrams into milligram-equivalents
- IV. Tables for converting milligram-equivalents into milligrams
- V. Tables for converting oxides to ions
- VI. Tables for converting nitrogen into nitrogen-containing ions
- VII. Table for converting milligrams of NH_3 into milligrams of NH_4^+
- VIII. Table for converting oxidizability with milligrams of KMnO_4 into milligrams of O

Factors for converting the results of water analysis from one form into another

Average value of activity coefficient f_{av}

Nomogram for calculating percent-equivalents

Nomogram for calculating pH from given values of free CO_2 and HCO_3^-

Calculation of aggressive carbon dioxide

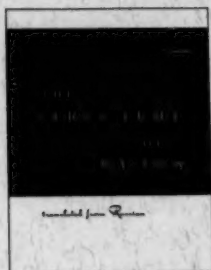
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